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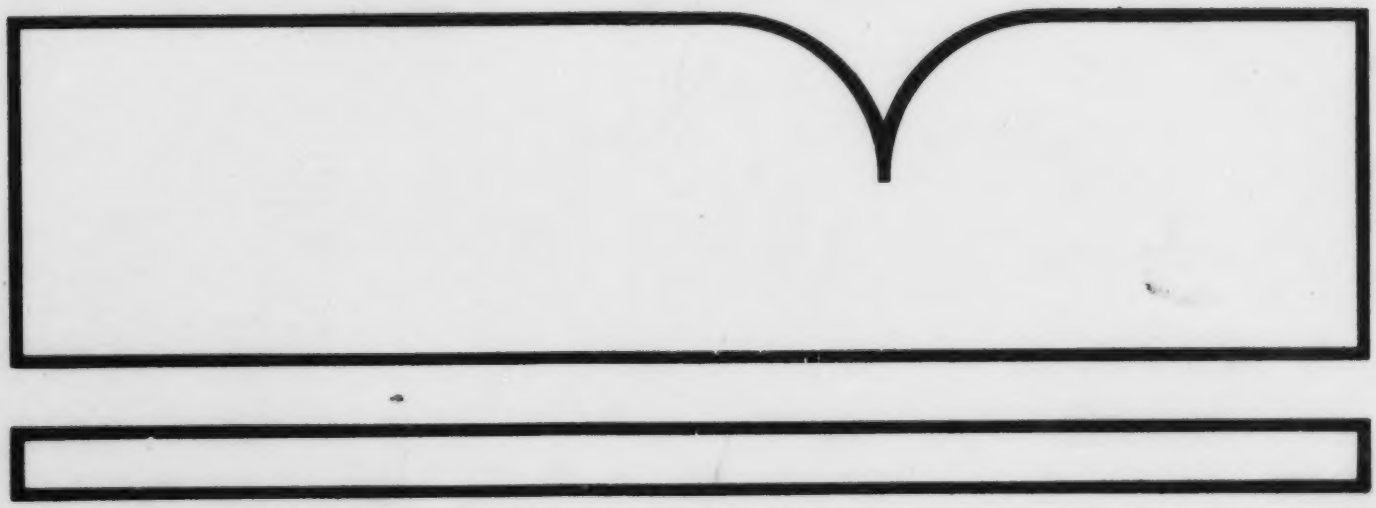

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DETERMINATION OF DRY DEPOSITION RATES FOR OZONE

by

Elmer Robinson
Brian Lamb
M.P. Chockalingam

Air Pollution Research Section
Chemical Engineering Department
Washington State University
Pullman, Washington 99164

EPA Grant R805342

Project Officer
William Lonneman
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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16. ABSTRACT

The report presents ozone (O_3) velocity deposition (V_d) measurements over three different vegetation types at three different geographic locations in the United States. The purpose of this study was to relate V_d measurements of ozone to more commonly measured meteorological parameters over a wide range of ambient conditions. In this way a general calculation procedure could be developed for ozone V_d to be used in pollutant transport models. The results suggest that a general relationship can be developed between V_d and the lateral qustiness parameter $\sigma_\theta u$, where σ_θ is the standard deviation of wind direction and σ_θ is the average wind speed. The relationship given in the form of the power curve $V_d = a(\sigma_\theta u)^b$ must be adjusted for terrain and vegetation type. The report also must be adjusted for terrain and vegetation type. The report also presents data to suggest that ozone V_d over forested areas are 2 to 3 times greater than over grassland areas.

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ABSTRACT

This research program has been directed toward measurements of the rates of loss of ozone from the atmosphere onto the earth's surface under non-precipitation conditions. This is commonly called "dry deposition" and the critical parameter is usally the "deposition velocity", V_d. Studies by a number of other investigators have evaluated the general magnitude of V_d for ozone as being about 0.6 cm sec^{-1}. The major objective of this present research was to measure ozone V_d and other meteorological parameters over a wide range of ambient conditions and then to relate the values of V_d to commonly measured or estimated meteorological parameters. In this way a submodel for ozone V_d could be developed for use in meteorological pollutant transport models.

The micrometeorological profile method for estimating V_d was used in this research program. Measurements were made over a soybean field in Illinois, a grain and grass field in Pullman, Washington, and a hardwood forest area in south central Pennsylvania. The results show that over the soybean and grain fields that V_d has a strong diurnal cycle and is correlated with the lateral gustiness parameter G, where $G = \sigma_\theta \bar{u}$; σ_θ is the standard deviation of wind direction and $\bar{u}$ is the average wind speed. The model is of the form $V_d = aG^{-b}$ where the value of a was between 0.2 and 0.4 and b was between 0.7 and 1.3.

The measurements of V_d over the forest area did not follow this model and the reasons are not clearly identifiable. However there were considerable periods of unstable meteorological conditions during the experiment. There was little change in turbulence over the forest on a diurnal basis with conditions generally being turbulent over the forest canopy both during the day, as might be expected, and also, unexpectedly, at night. Values of V_d over the forest area were generally larger by a factor of 2 or more compared to the V_d measurements over the crop surfaces.

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CHAPTER 1

INTRODUCTION

Air pollutants are scavenged from the atmosphere to a major extent by adsorption or reaction at the earth's surface. These scavenging processes proceed both through precipitation processes and by non-precipitation or "dry" mechanisms. The effects of scavenging mechanisms usually have not been considered to be important factors in plume diffusion modeling because the model was applied to relatively short distances where the time periods would be too short for deposition to be significant. However diffusion and transport are now being modeled over much greater distances and much longer time periods. Under such conditions it is no longer prudent to ignore the scavenging phase of the transport model. For example, Husar, et al. (1978) in an assessment of long-range transport of SO_2 from a tall power plant stack estimate that roughly half of the emitted SO_2 is lost to the ground by dry deposition in 4 days of downwind travel.

Ozone is another pollutant that exhibits long-range transport. As a secondary urban pollutant ozone is of major concern in the downwind plumes from major urban areas such as Los Angeles, New York, or Washington D.C. The loss mechanisms for ozone are not as well identified as for SO_2 but it is likely that the dry deposition process is as much a factor in the downwind flux of ozone from an urban area as it is for SO_2 in a power plant plume.

This research program has dealt mainly with atmospheric ozone and its rate of deposition under a variety of conditions. The objective of the research was to develop a model of the ozone deposition parameter "deposition velocity" that would facilitate the incorporation of the deposition scavenging process into urban dispersion models. To carry out this research an extensive program of field measurements was conducted. These

measurements stressed continuous measurements of the various micrometeorological parameters which are necessary for the calculation of the deposition velocity. These parameters were augmented with other meteorological measurements to provide a link between the deposition velocity and parameters of the Gaussian plume model.

The field measurement program was conducted in several major phases in 3 different locations. In July and September, 1977 measurements were made at Robinson, Illinois (near Terre Haute, Indiana). This was followed by a program in Pullman, Washington from April to July, 1978 and near Lancaster, Pennsylvania in July-August, 1979. At these 3 locations, the underlying surfaces were different. In Illinois the measurements involved a soybean field at 2 stages in its growth cycle while in Pullman the surface was grain and grass. The measurements in Pennsylvania were made over the top of a deciduous forest area with a 20 m high canopy. The result has been an extensive set of dry deposition and meteorological data to apply to modeling programs.

CHAPTER 2

DEPOSITION VELOCITY CALCULATIONS

The concept of a "deposition velocity", V_d, was first described in a 1953 paper by A. C. Chamberlain and R. C. Chadwick from the Atomic Energy Research Establishment, Harwell, Great Britain, as a means of explaining the loss of material from the atmosphere to the underlying surface when the material was too small to be covered adequately by Stokes' law. By definition, V_d is the coefficient that relates air concentration, C, to the deposition rate, D; thus

$$D = V_d C \tag{1}$$

where, D, the deposition rate, is essentially the downward flux of the pollutant ($\mu g\ cm^{-2}\ sec^{-1}$); and C, the concentration of pollutant can be expressed in $\mu g\ cm^{-3}$. Hence, the dimensions of V_d must have the units $cm\ sec^{-1}$ in order for the expression to balance. Since these are the dimensions of 'velocity' it was natural to label the coefficient "deposition velocity." It should be noted that V_d, because of its dependence on the concentration C, is not a fixed quantity and numerical values of V_d will depend on the height along the concentration profile at which the value of C is measured. In this program C was determined at the geometric mean height of the profile. For the 5 m profile studies over low crop surfaces this height is 141 cm. In other research studies reference heights of 1 to 2 m have been typical (e.g. see: Whelpdale and Shaw, 1974 and Garland, 1978).

Further study along these lines has shown that the deposition onto a surface is equal to F, the downward flux to the surface, and the F can be expressed in terms of well known micrometeorological variables and the vertical concentration profile. Thus,

$$F = K_m \frac{dC}{dz} \tag{2}$$

where K_m, is the eddy diffusivity coefficient for momentum and $\frac{dC}{dz}$ is the concentration gradient. K_m can be evaluated as:

$$K_m = \frac{\tau}{\rho} \left(\frac{du}{dz}\right)^{-1}$$

or

$$K_m = u_*^2 \left(\frac{du}{dz}\right)^{-1} \qquad (3)$$

where u_* is the friction velocity determined from surface stress, τ and air density, ρ, as

$$u_*^2 = \frac{\tau}{\rho}$$

It is assumed that momentum flux is equivalent to mass flux; thus

$$V_d = \frac{F}{C}$$

and V_d can be expressed as

$$V_d = \frac{u_*^2}{C} \left(\frac{du}{dz}\right)^{-1} \left(\frac{dC}{dz}\right) \qquad (4)$$

where C is the pollutant concentration at the geometric mean height, z.

In the WSU field studies, friction velocity, u_* is calculated from a logarithmic wind profile, using the relationship

$$\bar{u} = u_* \ln \left(\frac{z-d}{z_o}\right) \qquad (5)$$

where k is von Karman's constant and z_o is the surface roughness and d is the displacement height. Using equations (3) and (5), it can be shown that

$$K_m = u_* kz \qquad (6)$$

It is generally accepted that equation (6) is valid only for a neutral atmosphere.

It has been one of the major aims of micrometeorological research in the past several years to investigate the influence of atmospheric stability on atmospheric turbulence in layers close to the earth's surface. Stability of the atmosphere has direct relevance to the transfer of pollutants, because it affects the turbulence mechanism. It is an obvious fact that the temperature lapse rate in the lower portion of the atmosphere has a great influence on the vertical motion of the air. When neutral stability exists in the atmosphere the temperature lapse rate is adiabatic

and the vertical motion of air is not affected by buoyancy forces. During unstable conditions, the lapse rate is superadiabatic and the buoyancy forces enhance the vertical motion of air. However, when very stable conditions occur in the atmosphere, air temperature increases with height and the buoyancy forces resist vertical motion and thus exert a limitation on the mixing of air parcels. A very stable situation may be either a radiation inversion due to cooling of the ground surface during nighttime or a subsidence inversion caused by synoptic-scale pressure gradients. Therefore, it becomes obvious that the temperature profile reflects the variation in the thermal stratification of the air on which the turbulent and diffusive properties are dependent.

Equation (2) is a flux-gradient relationship, where the flux of a property in the atmosphere is represented as a product of the gradient of the property and an eddy diffusivity coefficient such as K_m (for momentum), K_h (for heat) and K_q (for water vapor). The flux-gradient relationships are derived from an assumption that the vertical transfers of momentum and heat are fundamentally involved in the maintenance and suppression of the turbulent motion, and the magnitudes of these transfers in relation to the corresponding vertical gradients provide a measure of the diffusive power of the atmosphere (Pasquill, 1974). One of the primary purposes of measuring the wind profile is to derive a measure of the vertical transport for momentum. The Reynolds analogy assumes that $K_m = K_h = K_q$. An obvious generalization of the Reynolds analogy would equate either of these three diffusivity coefficients to that of a pollutant, namely, K_c.

It is an established hypothesis in micrometeorological literature that the logarithmic wind profile is valid only for neutral stability conditions in the atmosphere and that it is not reliable for unstable or stable conditions. In a neutral atmosphere, the diffusivity coefficient for momentum, K_m, is equal to the diffusivity coefficient for heat, K_h. Under stable and unstable conditions the assumption of a logarithmic wind profile is not valid because of buoyancy considerations and there are two factors that should be considered: (1) the relationship indicated in equation (6) needs a correction and, (2) the diffusivity coefficients for momentum, heat and water vapor cannot be considered identical. There have been several efforts to define precisely the functional relationships between stability

parameters and the correction factors to be used in the estimation of the three diffusivity coefficients under non-neutral conditions in the atmosphere (Wesely and Hicks, 1977).

A generally accepted method for introducing stability correction factors in the flux-gradient relationships (Dyer, 1964) is the use of the Monin-Obukhov universal functions ϕ_m, ϕ_h, and ϕ_c as described below:

$$\phi_m = \left(\frac{kz}{u_*}\right) \frac{d\bar{u}}{dz} \tag{7}$$

where ϕ_m is the dimensionless gradient of momentum

$$\phi_h = (\rho C_p k u_* / Q_h) \frac{d\theta}{dz} \tag{8}$$

where

ϕ_h: Monin-Obukhov function for temperature
c_p: specific heat of air at constant pressure
Q_h: sensible heat flux
θ: potential temperature of air

It is commonly assumed that ϕ_c for pollutant concentration is analogous to ϕ_m or ϕ_h, hence:

$$\phi_c = (k u_* / F) \frac{dc}{dz} \tag{9}$$

Dyer (1974), has recommended the use of the following empirical relationships, as approximations for the respective ϕ-functions.

$$\phi_m = (1 - 16\ z/L)^{-0.25}, \quad z/L < 0 \tag{10}$$

$$\phi_m = (1 + 5\ z/L), \quad z/L > 0 \tag{11}$$

$$\phi_h = (1 - 16\ x/L)^{-0.5}, \quad z/L < 0 \tag{12}$$

$$\phi_h = (1 + 5\ z/L), \quad z/L > 0 \tag{13}$$

where, L is the Obukhov length scale of turbulence near the surface estimated from the following equation:

$$L = - \rho c_p u_*^3 \theta\ [\ kg(Q_h + LE/14)]^{-1} \tag{14}$$

An approximation to equation (14) will be,

$$L = - \rho C_p u_*^3 \theta / kg Q_h \tag{15}$$

where the flux term of latent heat of evaporation, LE, has been ignored. Equation (15) has been used, in this study, for the estimation of L. To explain the terms in equation (15), θ is the potential temperature at the

geometric mean height, z, at which the Obukhov length scale, L, is estimated. The general equation for the temperature profile is,

$$\frac{dT}{dz} = \frac{T^*}{kz}$$

or

$$T_z = -\frac{T^*}{k} \ln\left(\frac{z-d}{z_T}\right) = a' + b' \ln (z-d) \qquad (16)$$

where T_z is the air temperature at height z, T^* is the scale temperature analogous to friction velocity, and a' and b' are constants. The sensible heat flux, Q_h, can be estimated as follows:

$$Q_h = c_p \rho(-T^*)\, u_* \qquad (17)$$

we have assumed, as have others (Shreffler, 1978; Hicks and Liss, 1976) that pollutant flux is generally analogous to the flux of heat and moisture rather than momentum, under atmospheric stability conditions other than neutral. Therefore, ϕ_h may be used as a stability correction factor to equation (4), and the equation for V_d becomes,

$$V_d = \frac{u_*^2}{C}\left(\frac{du}{dz}\right)^{-1}\left(\frac{dC}{dz}\right)\phi_h \qquad (18)$$

$$= \frac{u_*\, k\, z}{C}\left(\frac{dC}{dz}\right)\phi_h \qquad (19)$$

The factor ϕ_h is chosen from equations (12) and (13) according to the value of z/L as indicated.

The expression for flux will be,

$$F = V_d\, C \qquad (20)$$

CHAPTER 3

EXPERIMENTAL PROGRAM

The objective of this experimental program was primarily to measure the dry deposition rate for ozone, O_3. Subsequently some exploratory measurements were made involving both SO_2 and several hydrocarbons. The results were inconclusive and are not covered in this report. A second objective was to relate the deposition rate for O_3 to a wind or a gustiness parameter such as σ_θ for inclusion in gaussian-type plume models. As mentioned previously, the profile method was selected as the V_d estimation technique.

The field system for the profile measurements consisted of four major components: (1) an instrumentation tower of either a scaffold type or taller antenna-type as a mounting for profile measurements of meteorological parameters and air quality concentrations, (2) the meteorological sensor system, (3) the air sampling system and, (4) a field facility to house the instrumentation to support the field program. Details of the field operations are given below.

EXPERIMENTAL SITES

Field studies were conducted at Robinson, Illinois; Pullman, Washington; and near Lancaster, Pennsylvania.

The Robinson, Illinois field study began July 15, 1977 with the installation of meteorological and air sampling instruments adjacent to the Robinson, and continued up to July 31, 1977. A similar experiment was conducted at the same site from September 5 to September 15, 1977. Sampling for SO_2 was attempted but concentrations were below the sensitivity of the SO_2 analyzer available at that time.

The Robinson airport site was located about 10 miles east of Robinson, Illinois. The scaffold instrumentation tower was erected at the eastern edge of a soybean field. Because of the expanse of flat agricultural lands extending several miles upwind to the west, winds blowing from the directions of south through west to north were generally applicable to profile experiments and especially winds from the sector enclosed between 225° and 360°. Due to the location of buildings and other obstructions in the northeast, east, and southeast directions from the tower, wind blowing from these directions could not be considered for profile studies. With these exceptions, the experimental site was satisfactory for profile studies. The most frequent winds were from westerly directions and would satisfy the experimental requirements that the wind and pollutant flow be stabilized over an 'infinite uniform' surface before reaching the tower location and the profile sensors. The crop surface in the direction of the prevailing wind was actively growing soybeans which were about 75 cm high during the July experiment and 95 cm during the September 1977 study.

The second phase of field study program was carried out during between April 1 and August 7, 1978 on a site located about three miles northwest of Pullman, Washington. The site was selected on the basis of several considerations such as the predominant wind direction in the area, whether the ground surface would satisfy the general uniformity requirements necessary for profile studies, and whether local terrain features that would influence the measurement of micrometeorological variable could be avoided. At this Pullman site it was necessary to erect the experimental tower on the gentle slope of a hill which forms a shoulder of a shallow valley located in the midst of rolling hills. The prevailing wind blowing from the southwesterly direction would be along the axis of this shallow valley and satisfied in a reasonable manner the requirements that the wind flow be stabilized over an 'infinite uniform' surface. Although low hills with gentle slopes rising about 30 m above the valley axis were located about one half mile southwest of the tower the general terrain conformed more or less to a uniform formation which ensured a stable fetch of wind for a distance of about 5 to 10 miles. No trees or wind breaks were present along the prevailing wind direction. However, it is obvious that the site chosen in Pullman, Washington was a contrast to the site in Robinson, Illinois, with respect

to terrain features. At the Pullman site, the crop surface was a mixed growth of grain, grass and weeds having an average crop height of about 30 cm at the beginning of the April 1978 experiments described in this report.

The Pennsylvania forest site was on Tower Mountain between Lancaster and York. The tower was set up at the edge of a predominantly oak forest with a canopy height estimated to be about 20 m. To the west, in the direction of the prevailing wind, the forest had a relatively uniform surface for about 2 km. For the ozone deposition studies, profile data were used only when the wind had a fetch across the forest area. From the edge of the forest area where the tower was located the ground was cleared and level. The topography of Tower Mountain in the vicinity of the experimental site was generally flat for about 2 km around the site, but even beyond that distance there were no rapid changes in elevation in the area. Although the upper surface of the canopy appeared to be uniform some irregularities of 2 or 3 m could be observed as a few scattered tall trees extended above the average canopy height estimated to be about 20 m. The instrumentation profile extended 12 m above the average canopy top and with a uniform upwind fetch of about 2 km the site was considered generally appropriate for flux profile measurements. Droppo and Hales (1976) have discussed site selection problems. Thom (1975) has pointed out that in forest canopy situations the top of the canopy is the most relevant surface to be considered in exchange models.

FIELD LABORATORY

At each site the O_3 analyzer, pump system controls, and data recording equipment were housed in a field facility located so as not to adversely affect the profile studies. For the Robinson, Illinois study a small camper on a pickup truck was used for this facility. At the other sites small travel trailers served as a field site base. At each site standard 115V AC power was brought from an adjacent power line.

EXPERIMENTAL TOWERS

When the experimental site was covered with a low agricultural crop, commercial steel scaffold components were used to provide a tower at the experimental site. In these cases, in Illinois and at Pullman, the tower height was about six meters. Meteorological sensors were fixed on 2.5 m, 2.5 cm diameter supporting arms extending from the tower and positioned at levels of approximately 25 cm, 75 cm, 200 cm, and 500 cm above the crop surface. The meteorological sensors and air sampling intakes were located about 2 m out from the structure in the direction of the prevailing wind.

In order to match the temperature and wind measurements the wind sensors were fixed at the end of the supporting arm at the same height and distance as inlets of the temperature sensor shields. The aerodynamic influence between the tower and the sensors was considered to be negligible. Table 1 lists the arrangements of the instruments and sampling inlets on the scaffold profile tower.

The taller antenna tower was used for the 1979 deciduous forest experiment in Pennsylvania where the 20-m canopy height could not be reached by the scaffold systems. The antenna tower was assembled on the ground with the instruments and sampling lines in place. It was then tilted into position using a gin pole and winch with the supporting guy cables used to maintain a stable attitude during the lift. Figure 1 illustrates the instrument locations and relative heights of the sampling locations for this system. In general the instrumentation pattern for the forest study was similar to that followed with the lower crop surfaces.

MICROMETEOROLOGICAL SYSTEM

As described in the previous section, the wind sensors were fixed at various levels along the profile heights for the measurement of wind speed and wind direction. Care was taken to align the wind sensors and to ensure that the axis of the sensor shaft was truly vertical. The wind instrument system obtained from Climet Instrument Co. consisted of cup anemometers for the measurement of wind speeds and single-tail wind vanes for the measurements of wind direction. As shown in Table 1 the temperature and dew point

TABLE 1. Scaffold Tower profile instrumentation.

Level 1:	Crop Surface (approx.):	Air Sample Inlet
Level 2:	0.25 m*:	Air Sample Inlet, Wind Speed, Temperature, Dew Point
Level 3:	0.75 m :	Air Sample Inlet, Wind Speed, Wind Direction, Direction Sigma, Temperature
Level 4:	2.00 m :	Air Sample Inlet, Wind Speed, Temperature
Level 5:	3.00 m :	Air Sample Inlet
Level 6:	5.00 m :	Air Sample Inlet, Wind Speed, Wind Direction, Direction Sigma, Temperature, Dew Point

Solar radiation is measured on a continuous basis using a pyranometer at a height of 1.5 m.

*Profile heights are given relative to the top of the underlying vegetation.

Description of sensors:

Parameter	Sensor/transmitter model	Manufacturer
Wind speed	CL 011-2B	Climet Instruments Co. 1320 W. Colton Ave. Redlands, CA 92373
Wind direction	CL 012-6C	
Temperature	CL 016-1-015-5	
Dew point temperature	CL 016-2-015-12	

Signal Processing Unit: Climet Translator model CL-060

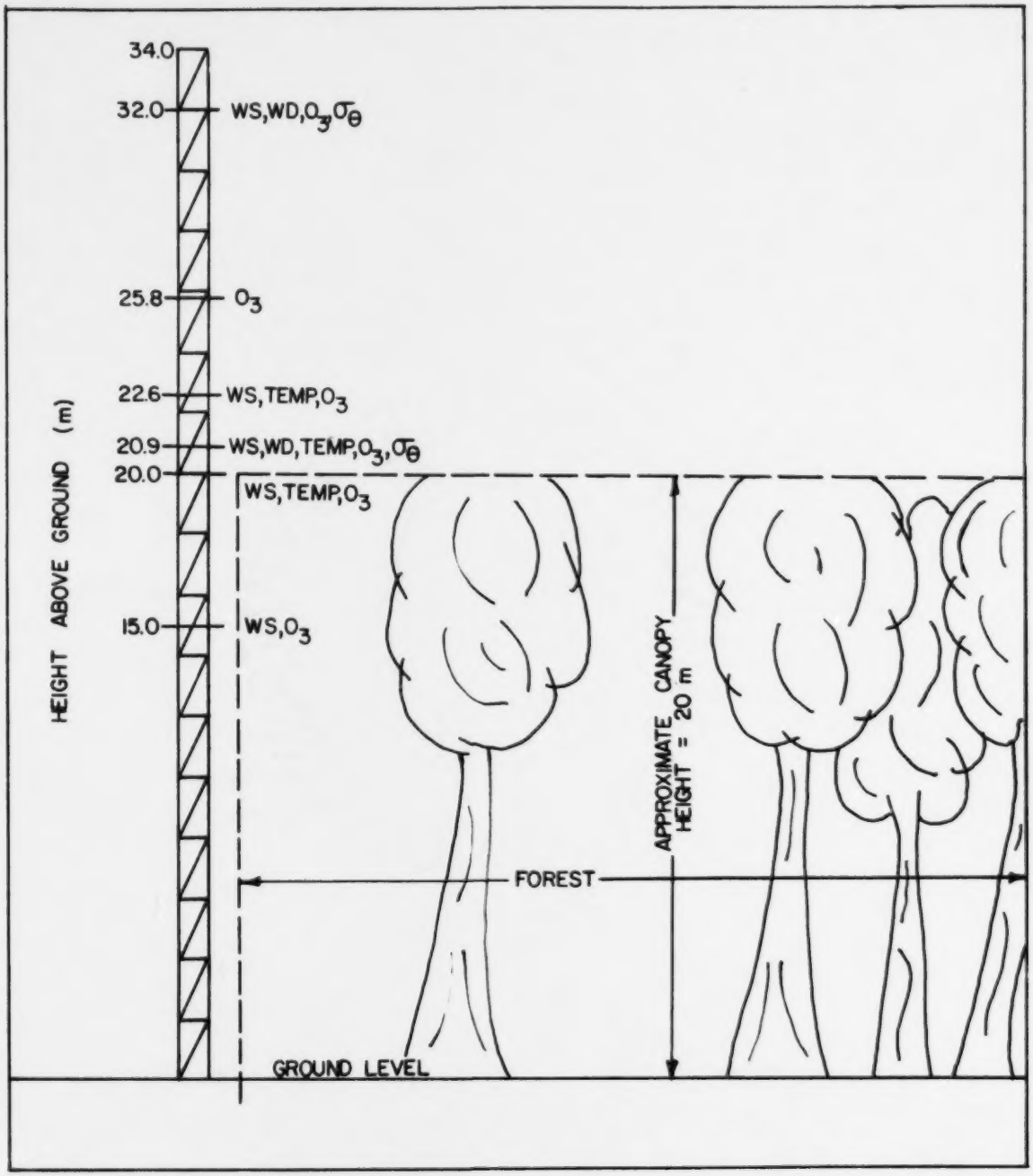

Figure 1. Antenna tower instrumentation for forest profile studies, Pennsylvania, 1979.

temperature sensors were fixed at various levels on the tower and closely matched the wind sensor heights. The usual precautions were taken in order to eliminate insolation errors in the measurement of ambient temperature. The temperature sensors used in the study were shielded and motor aspirated platinum resistance thermometers and are considered to be sufficiently accurate for the intended purpose. The humidity sensors were lithium chloride chemical Dew Cells incorporated as an integral part of two of the motor aspirated temperature shield systems.

Leads from the sensors were connected to a Climet CL-060 translator for signal processing. The output from the translator was fed into a 24-channel, multi-point recorder and a magnetic tape data logger. The multi-pointrecorder printed out on a chart sequentially at 10-second intervals the values of the sensor analog output signals. The magnetic tape data were recorded essentially simultaneously for all channels at a preselected sampling interval, such as 1-minute.

AIR SAMPLING SYSTEM

Air samples for O_3 analysis were drawn as indicated in Table 1 from six different levels above the canopy surface using 0.5" O.D. (0.25" I.D.) Teflon tubing through a solenoid valve assembly into a common manifold leading from the tower to the mobile laboratory. A pump installed inside the mobile laboratory moved the sample air stream through the common manifold and the pollutant analyzer obtained its sample from this manifold. The pollutant samples were taken from a point on the manifold ahead of the pump. At the tower six different lines of approximately equal length were run between the various sampling levels and the solenoid valve assembly located at the base of the tower. By electrically sequencing and opening one valve at a time, it was possible to draw an air sample into the common manifold successively from each of the six sampling ports. Each valve was kept open for five minutes and the entire air sampling sequence of six air samples from different levels was accomplished in a period of 30 minutes. Thus, it was also necessary to average the wind and temperature profiles and other meteorological data to coincide with the O_3 profile time of 30 minutes. Short-time concentration cycles in the O_3 system also had to be

noted so that the corrections could be applied. The output from the ozone analyzer was recorded on a strip-chart recorder.

The solenoid valves used on the air intake line were made of Teflon. All the Swagelok fittings used along the air sample line were of stainless steel.

A Monitor Lab Ozone Analyzer Model 8410 was used for ozone measurements. This instrument employs the chemiluminescent reaction between ozone and ethylene as a detection technique. It has a lower detection limit of approximately 1 ppb. The response time (46 secs for 90% response) of the ozone analyzer was satisfactory for the experimental requirement since each air sample was analyzed for five minutes. Line loss for ozone through the manifold was determined and suitable corrections were applied to the measured concentrations.

CALIBRATION OF INSTRUMENTS

The ozone analyzer was calibrated against an ozone generator which was in turn calibrated using the standard KI method. The meteorological sensors were checked for calibration according to procedures indicated by the suppliers. Calibration curves supplied by Climet Instruments Co. were used to convert the Climet translator output voltages to the appropriate temperature, wind speeds, etc. At the commencement of each field study program all the wind speed sensors were fixed at the same height and wind speeds were recorded for a period of 24 hours to compare the performance of each sensor relative to the other invarious wind conditions. A similar procedure was used for the temperature sensors. This procedure was useful in confirming that the sensors did not have a bias-response to the same signal. After an experiment was begun data were collected continuously; thus it was assumed that calibrations did not shift significantly during a given field period. The field periods varied from 10 days to more than a month. Absolute sensor calibrations were not done.

Routine checks were made to ensure correct functioning of the sensors and the signal processing system during the field operations.

DATA ANALYSIS

In order to estimate an average profile for ozone applicable to the 30-minute sampling sequence in the Illinois and Pullman experiments, a graphical interpolation procedure was used. Essentially this procedure involved plotting the time sequence of the 5-minute ozone samples at each sampling height, connecting the concentrations at the same height with a smooth curve, and then adjusting the set of six concentration curves so that, as nearly as possible, they formed a mutually consistent pattern. The average ozone profile for a given 30 minute period was estimated to be the vertical concentration gradient indicated by the set of 6 concentration curves at a time midway through the 30 minute ozone sampling cycle. It is recognized that this procedure introduces a degree of variability into the system that cannot be easily quantified. However it seemed to be the best approach to use for our available facility. Other investigators have also been faced with having to deal with non simultaneous measurements (Droppo and Doran, 1979). In the subsequent discussion of the Pennsylvania forest experiment Figures 19 and 20 illustrate how sequential ozone mixing ratios can be integrated into a time-height cross section pattern. In the Pennsylvania forest experiment the concentration profiles were estimated directly from the recorded data points with a computer calculation of the best fit logarithmic concentration profile.

The meteorological data for the Illinois and Pullman experiments were averaged over the same 30-minute period as the ozone profile either by computer processing of the data logger tape or by manually averaging the multipoint recorder chart record. For the Pennsylvania tower study in 1979 the meteorological data were processed into 30-minute averages by a Monitor Lab 9300 data logging system.

The uncertainty in the dry deposition velocities can be determined from standard error propagation techniques. For this analysis, the uncertainty in the wind speed measurements was taken to be ±0.1 m/s and the uncertainty in the relative temperature measurements was estimated to equal ±0.03°C. Relative ozone concentrations were taken to be accurate to within ±0.5 ppb. The error in the displacement height was estimated to equal

±0.05 h (h = canopy height) and the error in the surface roughness was assumed to equal ±10%. Calculation of typical deposition velocities using these error limits for the crop studies gave an overall uncertainty equal to approximately ±36%. For the forest study similar calculations indicated an uncertainly equal to approximately ±30%. For low deposition velocities over the forest where the ozone concentration gradient was small, the estimated error was as large as ±90%.

CHAPTER 4

RESULTS AND DISCUSSION

INTRODUCTION

As mentioned previously, the principal objective of this research program was to develop techniques to estimate deposition velocity that could be incorporated readily into meteorological diffusion modeling. With such a procedure or submodel an investigator could estimate a value of V_d from the meteorological parameters of the diffusion system rather than selecting a value from a tabulation of prior research results.

The selection of ozone as the test material for this program was based upon at least two important considerations. First, ozone is an important air pollutant and it is involved in significant long-range diffusion problems. Second, because of the general background concentration of ozone in the atmosphere experiments on ozone deposition velocity could be conducted on a continuous basis without having to consider site orientation relative to an industrial pollutant source, such as is necessary with studies involving SO_2. It was, of course, assumed that the natural background ozone in a relatively clean atmosphere would have the same deposition cycle as does ozone produced by photochemical reaction processes in the air pollutant plume from an urban area. There is no evidence that this is not a valid assumption.

The experimental data included continuous measurements of wind direction (θ), wind speed (u), standard deviation of wind direction (σ_θ), temperature (T), and dew point (TD) at the several heights, see: Table 1 and Figure 1. In the assessment of the experimental data it appeared that combinations of σ_θ and u could be related to the calculated values of deposition velocity (V_d). The following discussion thus emphasizes these variables.

For convenience we will use the symbol "G" to indicate the "gustiness parameter" formed by the product $\sigma_\theta \bar{u}$.

JULY, 1977 EXPERIMENT: ROBINSON, ILLINOIS

Figures 2 and 3, and appendix Table 1 describe the set of data gathered over a soybean crop in Robinson, Illinois between 1555 hours, July 24, 1977 and 1025 hours, July 26, 1977. The values of G where $G = \sigma_\theta \bar{u}$, V_d, ozone flux and ozone concentration at 100 cm above the surface of the crop are listed in appendix Table 1. All of these parameters have been estimated based on a 30-minute averaging time. The diurnal variation of V_d and the gustiness parameters, G, during this period is shown in Figure 2. The diurnal variations of ozone concentrations and ozone flux at a height of 100 cm above the crop surface are shown in Figure 3.

As described in the previous discussion, the site in Robinson, Illinois was limited in that the profile data could be considered only when the wind was between 210° and 330°. During the 42-hour period between 1555 hours, July 24, and 1025 hours, July 26, 1977 described by Figures 2 and 3, the profile data were discarded when the fetch of the wind was outside this sector. Similar procedures were followed for all the profile data.

As shown in Figure 2, V_d varied widely from a low value of 0.03 cm sec^{-1} to a high value of 1.01 cm sec^{-1}. Nighttime values were generally in the range of 0.1 to 0.3 cm sec^{-1}, while daytime values were around 0.6 cm sec^{-1}. The ozone flux through the 100 cm level and toward the surface shows typical nighttime values of around 1×10^{11} molecules cm^{-2} sec^{-2} and daytime values in the range of 6 to 8×10^{11} molecules cm^{-2} sec^{-1}.

In Figure 2, the diurnal variation of G exhibits the expected diurnal cycle with lower values at night and higher values in daytime. It is also evident that there is a reasonable correlation between the gustiness parameter, G, and V_d. On July 24, 1977, beginning with 1555 hours up to 2055 hours, the turbulence level indicates a steady decrease on the average as can be seen from the trend of G. The same trend is reflected in the variation of V_d. Beginning from about 2255 hours, an increasing trend of G is indicated. This increase in the turbulence level is, to a significant

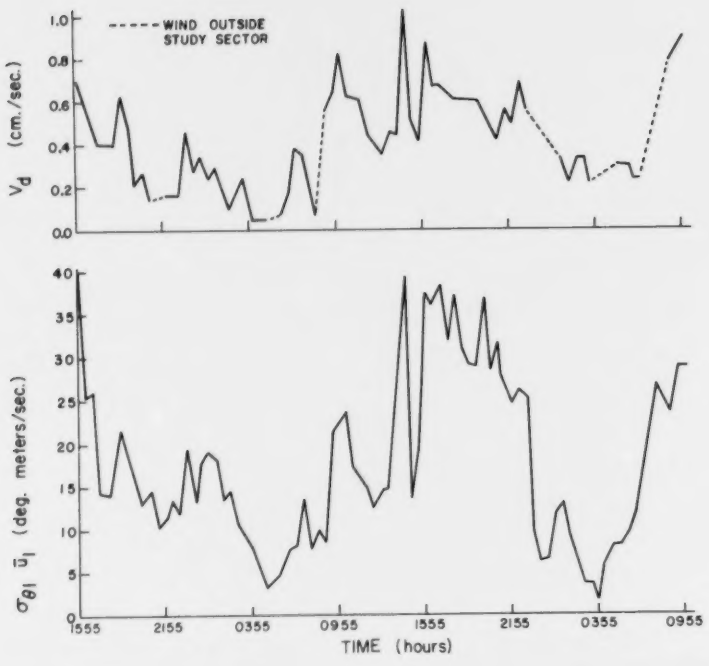

Figure 2. Ozone deposition velocity and gustiness ($\sigma_\theta \bar{u}$), July, 1977, Robinson, Illinois. Period: 07-24-77, 1555 hours to 07-26-77, 1025 hours.

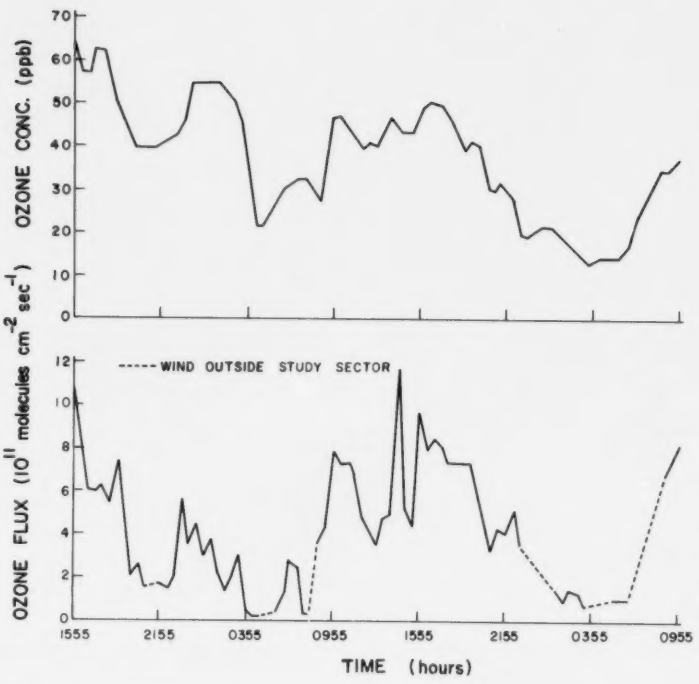

Figure 3. Ozone concentration and ozone flux. July, 1977, Robinson, Illinois. Period: 07-24-77, 1555 hours to 07-26-77, 1025 hours.

degree, reflected in the variation of V_d during the interval of time. Between 0055 hours and the next morning 0625 hours, both G and V_d indicate a low range of values. However, after sunrise, the steady increase in both G and V_d becomes obvious. The profiles recorded between 0825 hours and 0925 hours on July 25 were not considered because the wind direction was outside the acceptable experimental sector. The sudden increase in the turbulence level beginning about 0825 hours appears to be a typical forenoon situation of increasing convective activity. Thus following the G variation and the V_d trend, it becomes apparent that the turbulence level and V_d attained a maximum level around noon and remained high for a few hours in the afternoon. Beginning with a few hours after sunset, both G and V_d indicated generally a falling trend although the continued maintenance of turbulence at a significant level caused the V_d values to be somewhat greater than the usual nighttime values.

Most of the profiles recorded between 0225 hours on the night of July 25 and the next morning could not be included because of wind fetch considerations. The few periods of acceptable data are indicated.

Figure 3 shows O_3 concentration and O_3 flux data, both calculated for a 100 cm height above the soybean crop. The patterns are strongly correlated both between these two parameters and between the data in Figure 2. Figure 4, showing the correlation between the 64 available pairs of values of G and V_d, is considered to be a useful step in the development of a more generalized set of model values for ozone V_d. The log-log plot of these two parameters has a correlation coefficient of 0.75 (n=64) and thus provides a model for the estimation of ozone V_d from wind statistics. Since wind data can be obtained readily, either through direct measurements, or with the gustiness parameter by a model, a method seems to be available for estimating V_d. This will be discussed in more detail in a subsequent section.

Figure 4 includes data identified according to daytime, positive (upward) heat flux (open circles) and nighttime, negative (downward) heat flux (Δ symbol) conditions. The diurnal variation of V_d follows the trend of G. The scatter diagram, Figure 4, of the data gathered during different classes of stability as indicated by the heat flux shows a good

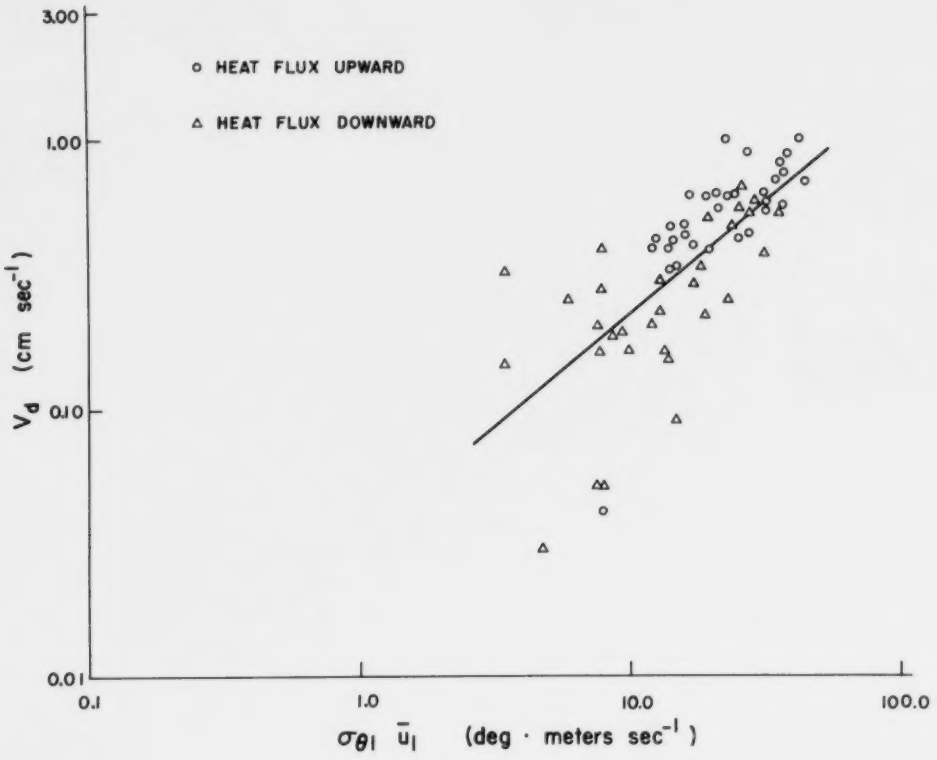

Figure 4. Relationship between gustiness parameter and V_d, July, 1977.

correlation for the range of G indicated. This is not surprising since it is expected that G would be sensitive to stability.

A general regression equation obtained between the turbulence parameter G and V_d for the July, 1977 Robinson, Illinois data is:

$$V_d = 0.0339\ (G)^{0.84}$$

where $G = \sigma_\theta \bar{u}$.

SEPTEMBER, 1977 EXPERIMENT:
ROBINSON, ILLINOIS

A second profile experiment was carried out at the Robinson, Illinois site in September, 1977 and the results are shown in Figures 5-8 and Appendix Table 2.

Figure 5 shows the diurnal variation of V_d during the 50-hour period between 1430 hours, September 9, 1977 and 1630 hours, September 11, 1977 over the soybean crop field in Robinson, Illinois. Figure 6 presents the diurnal variation of G during this same period. Ozone concentrations at 100 cm above the crop are presented in Figure 7, and the diurnal variation of ozone flux in Figure 8. The numerical values of G, V_d, ozone flux and ozone concentrations appear in Appendix Table 2. In general the pattern of V_d and the absolute values are similar to the July data with daytime V_d values being in the general range of 0.4 to 0.6 cm sec^{-1}. At night V_d was in the 0.02 to 0.1 cm sec^{-1} range. Values of the gustiness parameter, G, as shown in Figure 6 were higher on September 10 and 11 than was the case in July, as shown in Figure 2. Referring to Figure 8, it can be seen that significant flux to the surface occurs only in the daytime and this flux may vary from about 6 to 12 x 10^{11} molecules cm^{-2} sec^{-1}. This is the same general range as was found in the July data.

In Figures 7 and 8, it is indicated that a radiation or surface inversion occurred between 0000 hours to 0700 hours on September 10, 1977. The top of the inversion fluctuated around 4 meters, i.e. below the top point of the profile. During the occurrence of an inversion, the

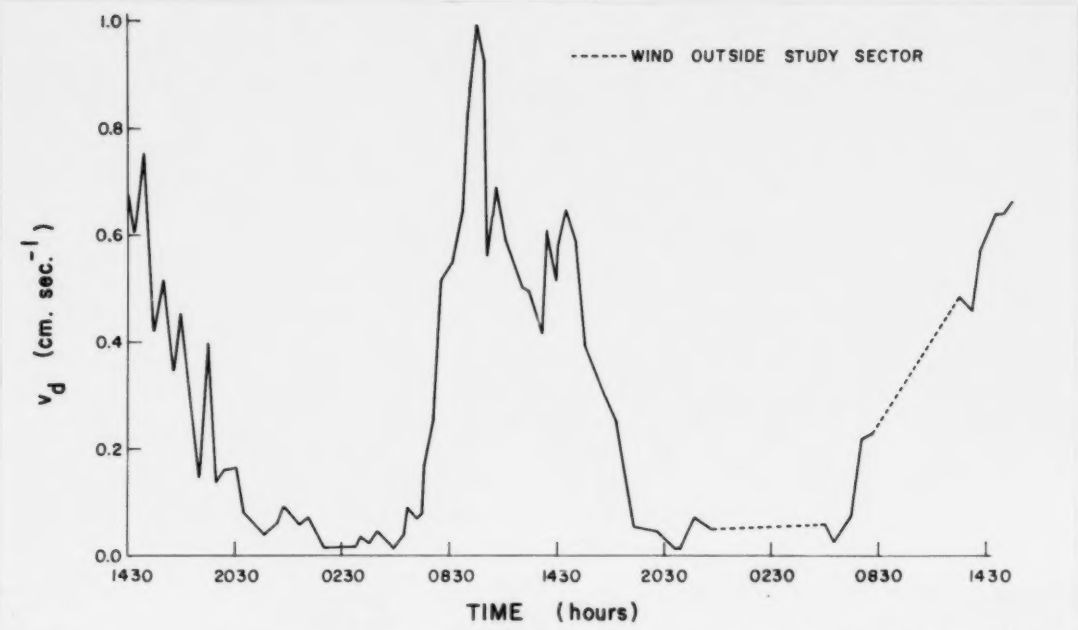

Figure 5. Diurnal variation of V_d. Robinson, Illionois, September, 1977. Period: 09-0977, 1430 hours to 09-11-77, 1630 hours.

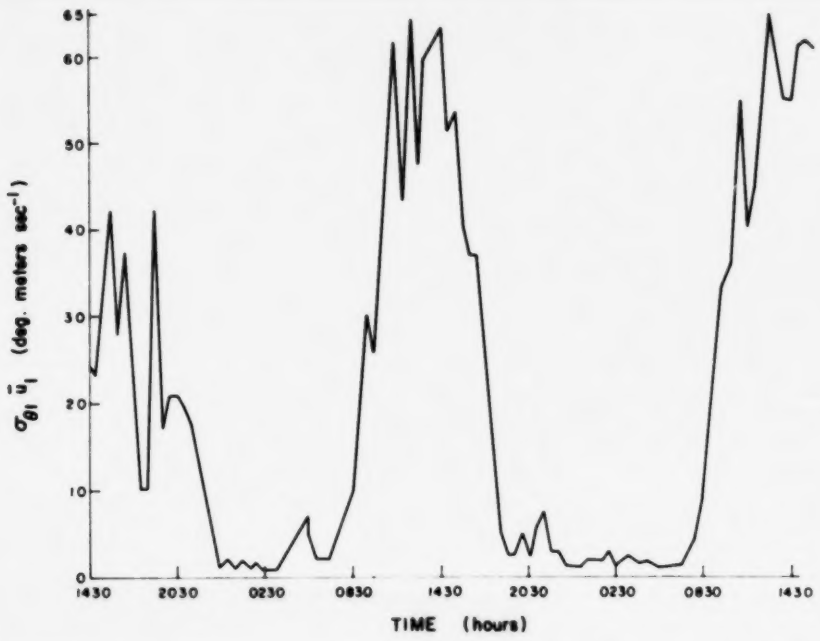

Figure 6. Diurnal variation of gustiness parameter. Robinson, Illinois, September, 1977. Period: 09-09-77, 1430 hours to 09-11-77, 1630 hours.

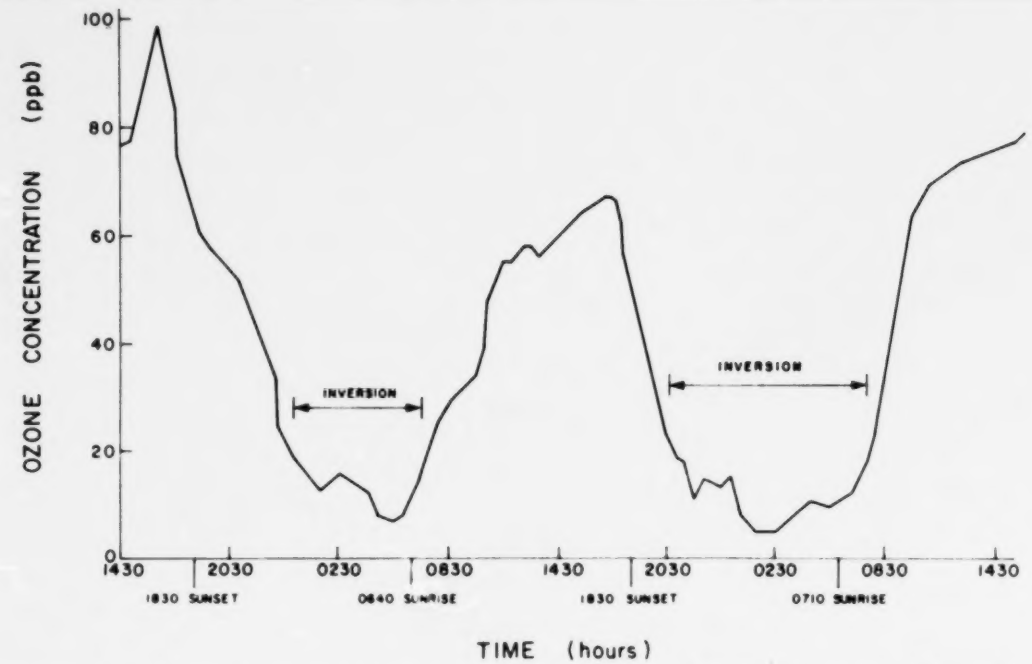

Figure 7. Diurnal variation of ozone concentration. Robinson, Illinois, September, 1977. Period: 09-09-77, 1430 hours to 09-11-77, 1630 hours.

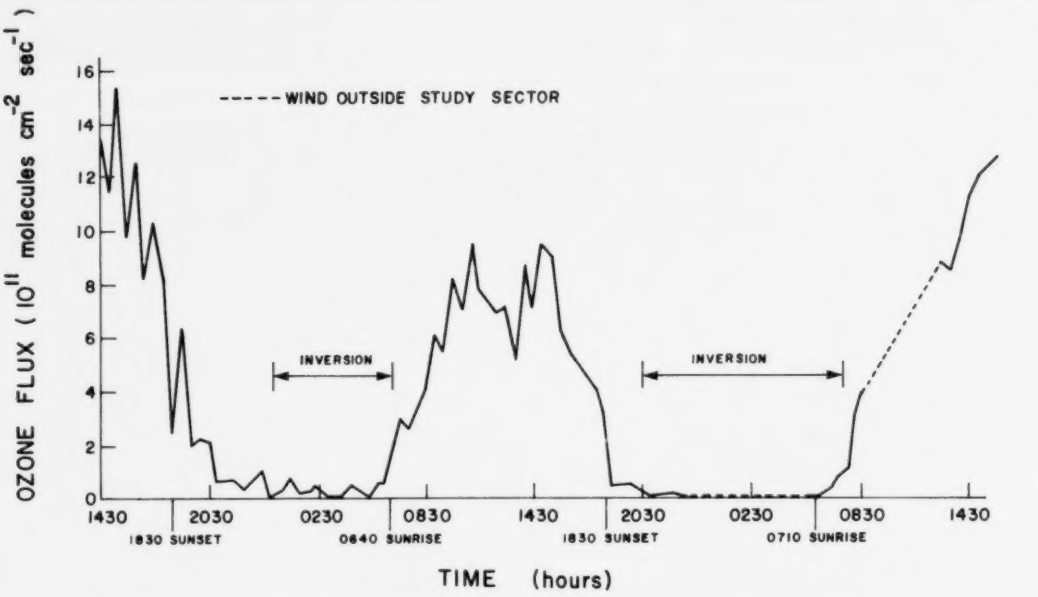

Figure 8. Diurnal variation of ozone flux. Robinson, Illinois, September, 1977. Period: 09-09-77, 1430 hours to 09-11-77, 1630 hours.

concentration profiles showed a discontinuity between the levels above and within the inversion layer. Garland and Derwent (1979) encountered similar situations. This was considered as a special case of layering and not in agreement with the necessary assumption of a constant flux boundary layer through the depth of the profile. In these low inversion situations the data recorded above the inversion were not included in the profile analysis. In an inversion situation the O_3 concentrations above the inversion were generally much higher than within the lower inversion layer and this situation could lead to a large concentration gradient between the 2 layers and a high calculated value of V_d for the surface layer. Since an inversion is a layer of very weak turbulent exchange in the vertical, a high value of V_d would be contrary to our present understanding of the physics of the situation. Garland and Derwent (1979) described the surface scavenging of O_3 within a surface inversion layer.

The second occurrence of a strong inversion was between 2030 hours, September 10, and 0730 hours, September 11, 1977. However, the data gathered during this period had to be discarded on the basis of the wind fetch considerations.

Figure 9 shows the September, 1977 relationship between V_d and G. The log-log regression is generally satisfactory with a correlation coefficient of 0.81, n=78. The regression expression obtained between the turbulence parameter G and V_d is,

$$V_d = 0.0241\ (G)^{0.78}$$

where $G = \sigma_\theta \bar{u}$.
There is general agreement between the July and September relationships found for V_d and G, as can be seen by comparing Figures 4 and 9.

1978 EXPERIMENT:
PULLMAN, WASHINGTON

In the spring and summer of 1978 a profile experiment was carried out over a growing grass and grain field near Pullman, Washington.

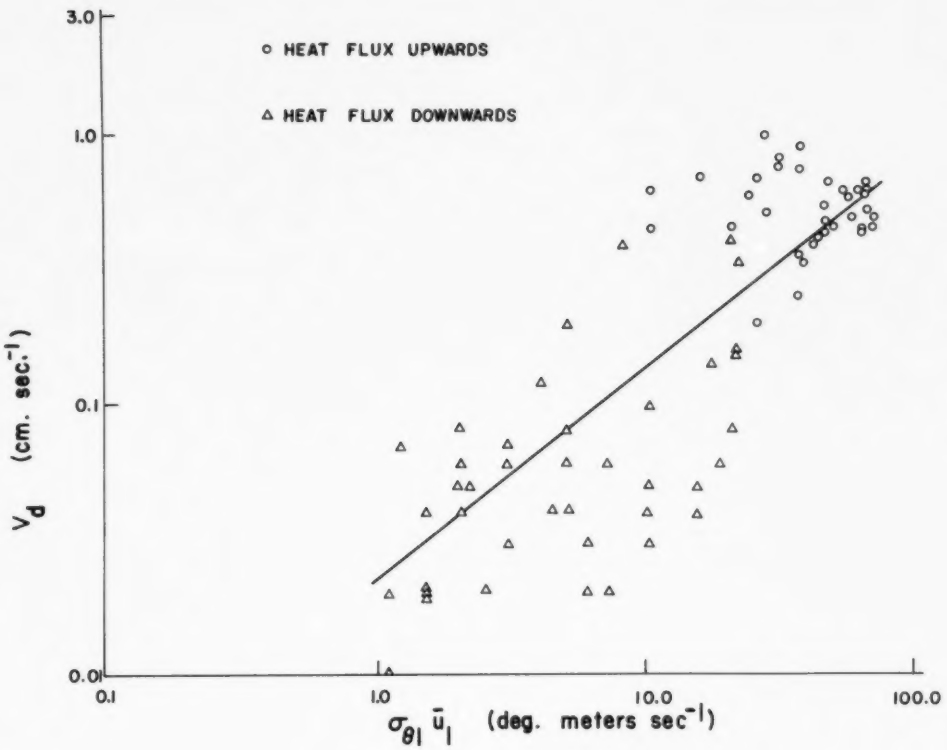

Figure 9. Relationship between gustiness parameter and V_d, September, 1977.

Figures 10, and 11 show the detailed V_d, ozone and gustiness data gathered at the Pullman experimental site during 2 days of this experiment, from 1500 hours, April 2230 to 2400 hours, April 24, 1978. The values of G and V_d, ozone flux and ozone concentrations are tabulated in Appendix Table 3. In Figure 10, the values of V_d in the daytime are generally between 0.4 and 0.6 cm sec^{-1}, the same general range as was seen in the Illinois data shown in Figures 2 and 5. However, the values of G generally tend to be smaller at the Pullman site compared to the Illinois data. Seasonal differences in both weather and air mass climate for the two experiments are such that these differences are not unexpected. The diurnal cycle is not as clear-cut in the Pullman data of Figure 10 as it was in the Illinois data, and significant values of both V_d and G occurred at night, especially the night of April 22-23. Less severe nighttime inversions during these spring days would be the logical explanation. Ozone flux in Figure 11 showed a strong diurnal cycle but with noticeably higher nighttime values of flux, about 1.0 to 2.0 x 10^{11} molecules cm^{-2} sec^{-1}, than were characteristic of the Illinois data. This obviously followed the pattern of V_d values. Daytime ozone flux to the surface was about 6 x 10^{11} molecules cm^{-2} sec^{-1}, generally equivalent to the Illinois data. The ozone concentration showed a decreasing trend during this period with a noticeable but weak diurnal cycle.

Figure 12 shows the relationship that was found for 80 pairs of values of V_d and G at Pullman for the 2 day period, April 22-24, 1978. The general equation obtained for this particular set of Pullman data is:

$$V_d = 0.0145\ (G)^{1.26}$$

where $G = \sigma_\theta \bar{u}$.

The correlation for this log-log relationship is 0.76. The slope of the Pullman regression shown in Figure 12 is somewhat greater than was found for the Illinois data, 1.26 compared to 0.84 and 0.78.

The extension of the Pullman experiment through the spring months of 1978 provided considerably more data than could be shown in Figures such as 10 and 11. The results of the evaluation of this more extensive data in

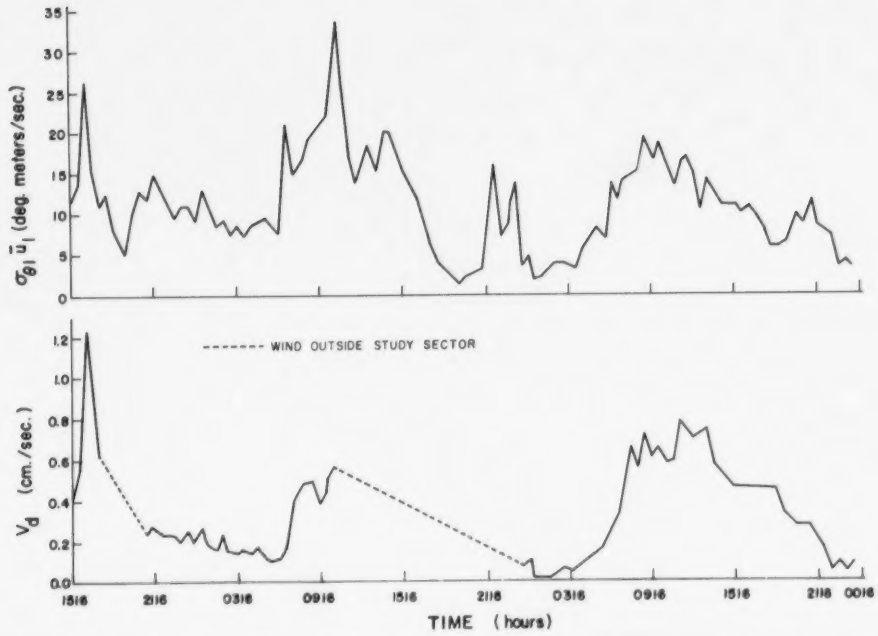

Figure 10. Variation of gustiness and deposition velocity. Pullman, Washington, April, 1978. Period: 04-22-78, 1516 hours to 04-25-78, 0016 hours.

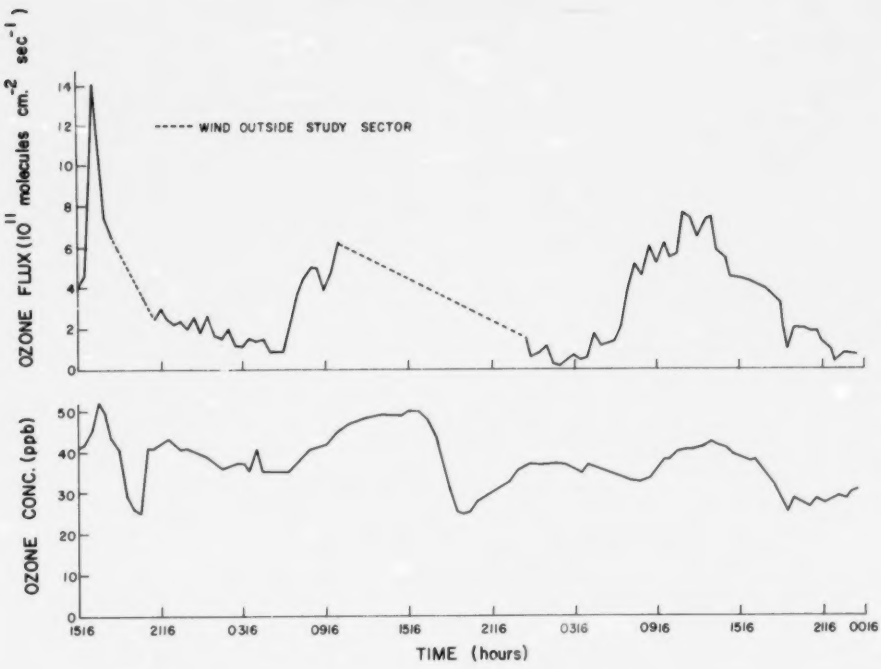

Figure 11. Variation of ozone concentration and ozone flux. Pullman, Washington, April, 1978. Period: 04-22-78, 1516 hours to 04-25-78, 0016 hours.

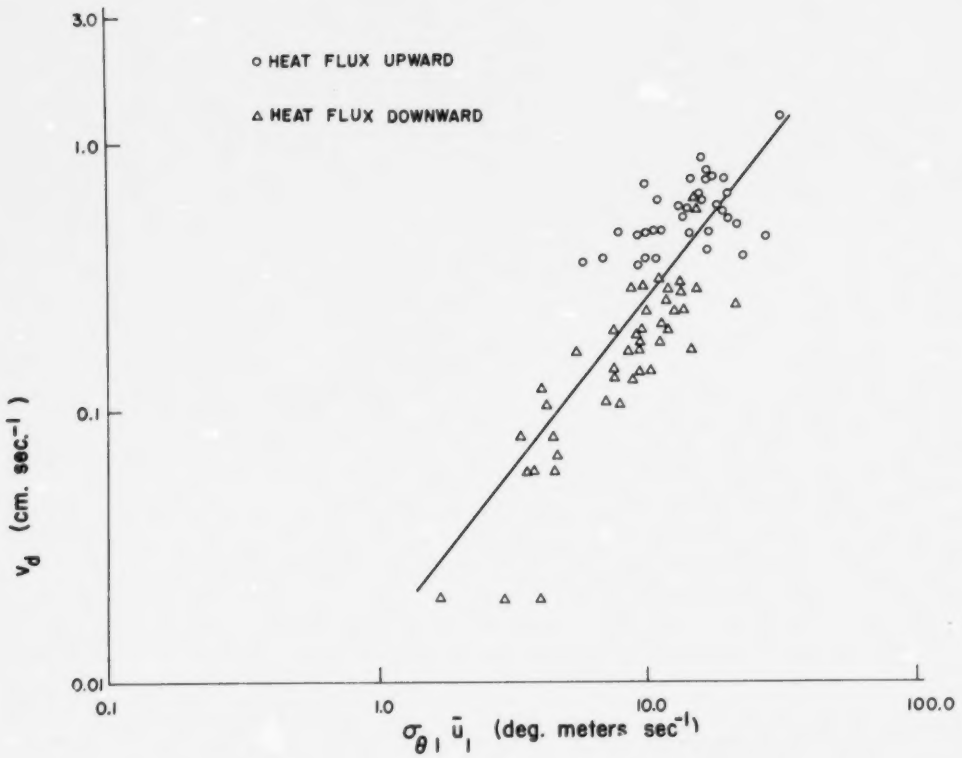

Figure 12. Relationship between gustiness parameter and V_d, April, 1978.

terms of a relationship between G and V_d are shown in Figure 13. This figure includes approximately a month of profile evaluations from April 22 through May 25, 1978. A total of 308 profiles are included in this experimental period. The regression equation for the Pullman data shown in Figure 13 is:

$$V_d = 0.0406\ (G)^{0.759}$$

where $G = \sigma_\theta \bar{u}$.
The correlation coefficient for this regression is 0.65. As noted above this expression applies to Pullman data obtained over more than a month of observations during a variety of late spring weather.

DISCUSSION

The experimental data shown here for ozone V_d values apply to a height of about 1 meter above the crop surface and show a general correspondence between the three experimental periods. At night, values of V_d were often close to zero except when the nighttime winds maintained some turbulence and prevented the formation of a strong radiation inversion. The typical daytime V_d value of around 0.6 cm sec^{-1} is similar to recent values published by Garland and Derwent (1979) in England and by Droppo and Doran (1979) in the United States. The nighttime V_d range of 0.1 to 0.3 cm sec^{-1} under situations when the surface based nocturnal inversion did not occur agrees well with the range reported for measurements in England by Garland and Derwent (1979). The range of ozone fluxes reported by Galbally (1968, 1971) and by Kelley and McTaggart-Cowan, (1968). The general trend of variation of V_d on a diurnal basis agrees with the trend indicated by Garland and Derwent (1979), indicating a daily cycle.

The trend of variation of the ground level ozone concentration exhibits a diurnal cycle with clearly defined daytime maxima and nighttime minima at both experimental sites, for the most part. This is a normal situation reported by several other investigators including: Garland and Penkett, 1976; Garland and Derwent, 1979; Samson, 1978; and Harrison, et al., 1978. Such behavior of ozone is attributed to the transport of ozone

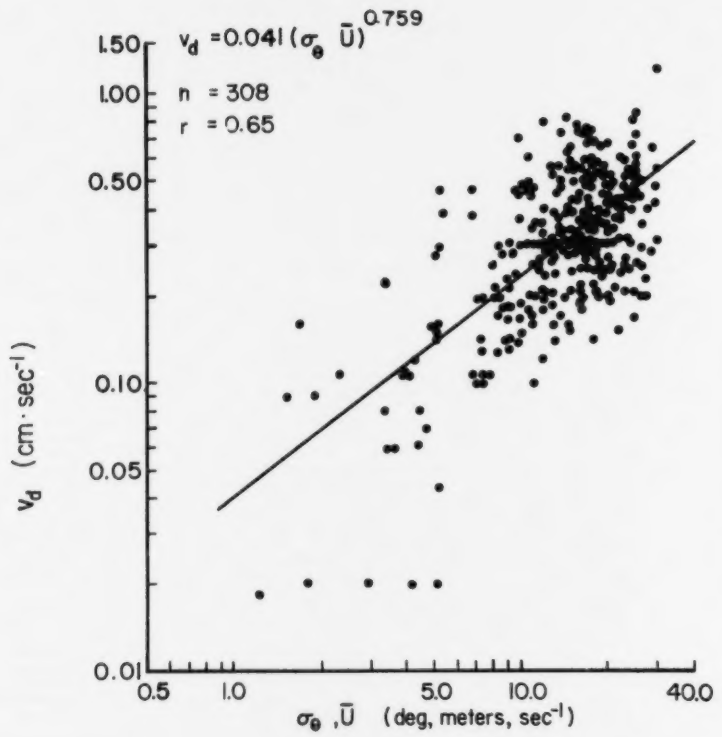

Figure 13. Relationship between gustiness parameter and V_d, April-May, 1978.

within and below the nocturnal inversion and destruction by deposition onto the underlying surface. The morning increase of ozone concentration is attributed to downward mixing of air from aloft when the radiation inversion is dissipated. In some situations photochemical ozone formation could play a role in morning concentration patterns.

The site at Pullman, Washington is a good example of a rural site not affected by any urban plume. The site in Robinson, Illinois, can probably be categorized as a rural site but with some reservations because of the refineries located about five miles west of the site and the general anthropogenic air mass contamination found in the midwest. However it is believed that these impacts were relatively small.

Two of the predominant factors in so far as the ground level concentration of ozone is concerned are turbulence aloft which enhances vertical mixing and photochemical reactions when solar radiation is available. Of these, the turbulence level mostly follows a diurnal cycle thereby increasing the probability of a high concentration of ozone during daytime. The photochemical production of ozone is obviously a daytime process. Considering these factors, a qualitative model can be described for the role of the dry deposition process as it relates to the diurnal ground level ozone concentration cycle.

We have used calculations of heat flux and in particular the direction of the flux, whether toward or away from the ground surface, as a means of dividing the diurnal cycle into surface heating and cooling phases. Values of V_d plotted as a function of G in Figures 4, 9, and 12 show that in general conditions of upward directed heat flux, such as would be typical of surface heating situations, had larger values of both V_d and the gustiness parameter, G. Downward heat flux conditions resulting from a cooling surface showed, in general, smaller values of both parameters. However there was not a clear separation of conditions on the basis of the direction of the heat flux, as can be seen from the overlap in the figures. The relations between heat flux values at the surface and the pattern of V_d onto the surface could probably be analyzed in more detail than has been done in our program.

During the daytime the ground level ozone concentration is a balance between the production rate, dry removal rate and the introduction of O_3

through mixing from aloft. As Junge (1962) pointed out with regard to O_3 having a source reservoir in the mid troposphere such as we have with background O_3, surface destruction will have a minimum effect on the ground level O_3 concentration when the daily maximum O_3 concentration occurs around midday. This is due to convective exchange, and surface layer replenishment is greatest at this time. Exceptions to the usual daytime situation can occur when an inversion layer persists through the day or when O_3 is formed within the surface layer. In a case of O_3 formation in the surface layer subsequent convective mixing would be expected to cause rapid dilution.

The normal nighttime case starts from a transitional situation when the heat flux reverses its direction around sunset and continues to be negative or upward until after sunrise the next morning. During this period the ground level concentration of ozone will be the net balance between the mass of ozone entering or generated within the shallow, stable surface layer and the dry removal rate, unless there is significant turbulence persisting through the night to maintain a downward flux of ozone into the surface layer. When a strong radiation inversion sets in, the isolation of the surface-based stable layer from the air above is quite effective. This inversion cycle has been observed on both the nights of September 9-10 and September 10-11, 1977 at the site in Robinson, Illinois. However, there are observed cases when significant ground level concentrations occurred during nighttime hours and these also need to be considered. These situations seemed to occur when significant mixing prevailed in the atmosphere, thus preventing the occurrence of a surface radiation inversion. An example for this case was observed in the data on the night of July 24-25, 1977 at the site of Robinson, Illinois (Figure 3). Also, on both the nights of April 22-23, and April 24-25, 1978 in Pullman data. Several investigators have analyzed situations where relatively high surface concentrations of ozone have occurred. The typical situation seems to be related to the presence of a nocturnal low level jet in the wind pattern. Such a jet can periodically break the surface stable layer and inject ozone-rich air into the surface layer from aloft. This model is consistent with our observations of periodic incidents of increased surface ozone concentration at night. Although we did not measure winds aloft, turbulence

increased during the incidents of increased nocturnal ozone, as indicated by Figures 2 and 3.

The similar log-log relationships between V_d and G shown in Figures 4, 9, 12, and 13 indicate that the wind and horizontal gustiness data can be used to approximate a value of ozone V_d for model calculations. These results indicate the V_d for O_3 is predominantly controlled by the surface layer turbulence and micrometeorology and the surface characteristics seem to be generally less important. This was also the conclusion of Garland and Derwent (1979).

An important point is whether a model such as the one correlating G and V_d could be useful in predicting the deposition rate. Dry deposition is a downward diffusion process, where as G is a parameter describing the lateral diffusion. However, G being a parameter that represents the turbulence through σ_θ would be indirectly related to the friction velocity u_*, a parameter that is essential in the computation of V_d. It is generally agreed that it is difficult to evaluate the friction velocity in the absence of a carefully recorded wind profile. In practical situations, especially in surveys conducted for environmental impact assessments, basic wind data would be gathered for an extended period of time; thus, wind data recorded at one measurement height would be available but not necessarily profile data. An estimation of the friction velocity would be impossible with the kind of data that are usually available for field use. Often, if it is needed, a friction velocity value is assumed. Sheih, et al. (1979) have used this approach to make regional estimates of SO_2 and sulfate deposition. In the present research program an effort has been made to model the deposition rate in terms of parameters that are usually available from the wind and other meteorological data that are collected for environmental assessment purposes. However, it should be pointed out here that the calculated V_d values presented in this report and used as a basis for our V_d model have been obtained originally from a rigorous treatment of the wind, temperature, and concentration profile data.

It has been common to consider the total transport mechanism to the surface as being analogous to a multilayer problem (e.g. see: Wesely and Hicks, 1977; and Shreffler, 1978). The several layers that are usually

identified are the aerodynamic layer, the surface layer, and for vegetation the stomatal or internal layer. In a multi-layer problem V_d can be considered as the inverse of the transport resistance and thus in total as the inverse of the sum of the several resistances to transport, or

$$V_d = \frac{1}{r_a + r_s + r_c}$$

where r_a is the aerodynamic resistance related to the micrometeorological turbulence in the boundary layer; r_s is the surface resistance describing the transport by molecular diffusion through the layer in direct contact with the leaf or soil surface, and r_c is the resistance to transfer through the stomatal openings on the leaf surface itself.

In our experiment we have related the total V_d value to the aerodynamic properties of the system, and thus we have made the tacit assumption that $r_s = r_c = 0$ for our experiments. Since our objective was to develop a procedure to estimate V_d for ozone from available meteorological measurements we did not explore in detail the impacts of the underlying leaf surfaces. Since our total numbers of individual measurements in the several experiments were relatively large, more than 500, and covered a variety of weather situations the effects due to a number of variables are represented in the data. Of course at this time the results should not be extrapolated to situations that are significantly different such as sparsely vegetated desert surface areas. Likewise, the lack of success in applying the G model to the Pennsylvania forest canopy in subsequent experiments may be due in part to the very much greater leaf area in the forest canopy compared to the crop surfaces studied initially. The SO_2 deposition model of Shreffler (1978) indicates the possible importance of canopy parameters in V_d values.

As indicated by Figures 4, 9, and 12 and the accompanying text our model for estimating V_d depends on an empirical relationship between V_d and the gustiness parameter, G. As indicated by Pasquill (1962) and Slade (1968), among others, G can be related to the intensity of turbulence, usually defined in the lateral (y) plane

$$i_y = \left(\frac{v'^2}{\bar{u}^2}\right)^{0.5} = \frac{\sigma_v}{\bar{u}}$$

where v' is the turbulent velocity deviation along the y axis and σ_v is the standard deviation of the y-axis velocity component. As shown by Slade (1968, pg. 46) the fluctuations of an azimuth vane, σ_θ, are related to σ_v by the relationship

$$\sigma_\theta = \frac{\sigma_v}{\bar{u}}$$

and thus

$$\sigma_\theta \bar{u} = \sigma_v$$

Therefore our gustiness parameter $\sigma_\theta \bar{u}$ or G is directly related to the turbulent dispersion in a plane horizontal to the ground. This parameter will be related to stability through the impact of stability on σ_θ under conditions of equal wind speed. Although in many cases including a significant part of our experimental program $\bar{u}$ is also a function of stability with lower values of $\bar{u}$ in stable conditions. However, there is no fundamental reason for this to occur and it cannot be generalized.

DISCUSSION OF FOREST CANOPY RESULTS

The Pennsylvania forest experiment in 1979 has been analyzed using analytical procedures that were similar to those used in the earlier studies in Illinois and at Pullman. During the 19 days of the forest canopy experiment there were a total of 188 hours when the wind fetch was satisfactory for the ozone deposition experiment and when all the necessary instruments were operational. It should be recalled that the instrument and profile tower was set up at the edge of the forest area and was not surrounded by the canopy. Since the forest canopy did cover 180° around the tower and the fetch of all experimental periods were well within this sector we do not believe the experiment was adversely affected by these features of the site.

In the forest canopy calculations some modifications needed to be made in the procedures compared to the low crops because it was necessary to introduce a significant zero plane displacement height, and to determine a roughness length, Z_o, for the forest surface. These terms appear in the logarithmic wind profile,

$$u = \frac{u_*}{k} \ln \left(\frac{z-d}{z_o} \right)$$

Values of these parameters were taken from the detailed study by Quarles (1981) in which he determined a value of d equal to 0.66 x canopy height or 13.2 m. (See: Quarles, et al. (1980) and Stanhill, 1969). The roughness length, z_o, of 2 m was calculated from the wind profiles obtained during the relatively few neutral stability periods observed during the experiment (Thom, 1975). Although the displacement height can also be calculated using neutral stability according to Thom (1975), there was not a large enough data base for such a calculation and the value of d was assumed to be 0.66 of the 20 m canopy height.

Analysis of the forest profile data showed a significantly different pattern than had occurred with the previous low crop experiments. First, average values of V_d were generally higher than for the crop land experiments, and in Pennsylvania the periods of low or near-zero values of V_d

were relatively infrequent. In addition the correlation between V_d and $\sigma_\theta \bar{u}$ or G was generally low. An analysis of the various meteorological measurements and the several calculated parameters showed that diurnal cycles evident in the data were relatively weak and that even at night the stability parameters of lapse rate and turbulence characteristically showed values that indicated unstable conditions existing in the layer above the forest canopy. Thus the meteorological conditions characterizing this experiment were significantly different than the previous studies.

Figures 14 through 18 show the hourly median values at the 20.9 m level, about 1 meter above the forest canopy, of wind speed ($\bar{u}$), horizontal gustiness σ_θ, ozone mixing ratio, deposition velocity V_d, and the gustiness parameter G. These median values relate only to those periods when the wind was across the forest canopy. In Figure 14 showing the 20.9 wind speed pattern, there is a weak diurnal cycle with maximum speeds of about 2 ms^{-1} between 1000 and 1600 EDT. Nighttime winds had median speeds of about 1 ms^{-1} between midnight and 0800. As shown in Figure 15 horizontal gustiness, σ_θ, at 20.9 m had median values in the lower range between 1900 and 0100 and peak values between 1400 and 1700 EDT. A value of about 26° would approximate an average daily median value. The diurnal pattern of median O_3 mixing ratio values at 20.9 m is shown in Figure 16. A strong diurnal cycle is present with the low values of about 50 ppb occurring between 0800 and 0900 EDT and peak values of about 110 ppb occurring in the mid afternoon between 1400 and 1800 EDT. Compared to the diurnal O_3 cycles seen in the Illinois and Pullman experiments these Pennsylvania O_3 values are significantly higher in the afternoon, probably indicative of strong photochemical formation. The minimum mixing ratio values are also relatively high compared to the other experiments where values would approach zero during the night and early morning hours. It has been concluded that the canopy boundary layer was generally a region of very active O_3 transport with the possibility of on-going formation and that it may not have approximated an equilibrium condition well enough to generally meet the experimental requirements for the deposition velocity determination. This will be examined in more detail subsequently.

The meteorological and O_3 profile data were used to calculate a value of O_3 deposition velocity, V_d, for the times when the wind was across the

canopy. Figure 17 shows the diurnal pattern of median hourly V_d values. The general daily trend is much less marked than was apparent in the Illinois and Pullman studies; however there is considerable variation from hour to hour, especially in the early morning hours.

Figure 18 is a plot of the median hourly values of the product $\sigma_\theta \bar{u}$ or G, the gustiness parameter that was found to be correlated with V_d in the low crop studies in Illinois and Pullman. There is a definite diurnal cycle to G with a maximum value at 1600 EDT, the mid afternoon. Minimum values occur in the early evening between about 1900 and 2200. However, compared to the previous low crop studies the values of these median G values are high with the minimum values being about 20 deg m sec^{-1} and maximum values being about 50 deg m sec^{-1}. During the low crop studies a value of 20 deg m sec^{-1} was characteristic of daytime conditions and a value of V_d of about 0.4 cm sec^{-1}. Pennsylvania daytime values of G of about 50 deg m sec^{-1} in the V_d general relationships found for the earlier data would correspond to a V_d value of about 0.8 cm sec^{-1}. Compared to the median V_d values shown in Figure 17 these calculated values based on the low crop experiments are low. The maximum daytime values for V_d shown in Figure 17 are about 1.2 cm sec^{-1} or 50% higher than the calculated value.

It is recognized, of course, that in the case of the forest the canopy height is not as close to the calculated level of zero wind speed, i.e. the sum of the displacement height and the roughness length, as it was in the field crop situations. For the Pennsylvania experiment the displacement height was estimated to be 66% of the canopy height or about 13 m (Quarles, 1981). With a roughness length value or 2 m, this places the hypothesized zero wind level at about 5 m below the canopy top and about 6 m below the first sensor station above the canopy, 20.9 m. In the previous crop surface studies the zero wind level was less than 1 m below the lowest profile point.

In a search for an explanation of how the Pennsylvania forest experiment might have differed from the previous low crop studies more detailed examinations were done of both the meteorological conditions and the ozone patterns. Meteorologically the boundary layer over the forest was characterized by turbulent flow conditions and was seldom if ever observed to have a temperature inversion structure or other characteristics of a stable regime.

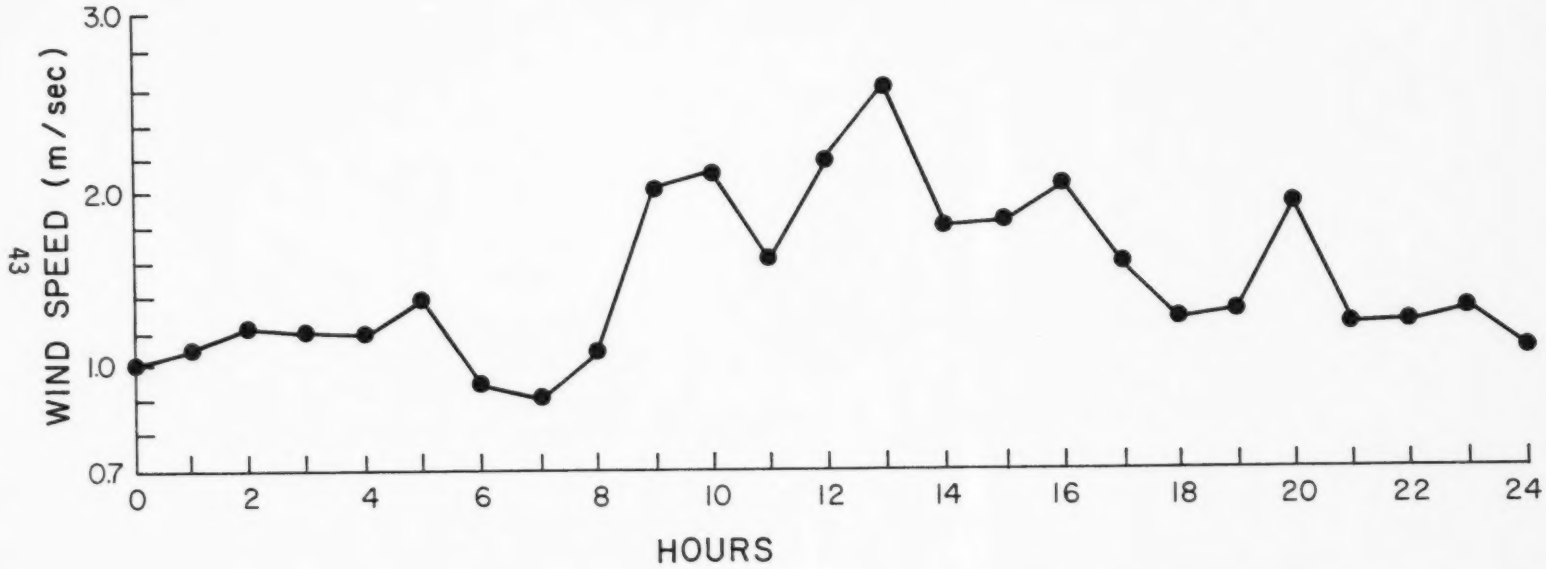

Figure 14: Median hourly Wind Speed for Deposition Velocity Experiments, Pennsylvania Forest Site, August 1979. (Note the non-zero base line)

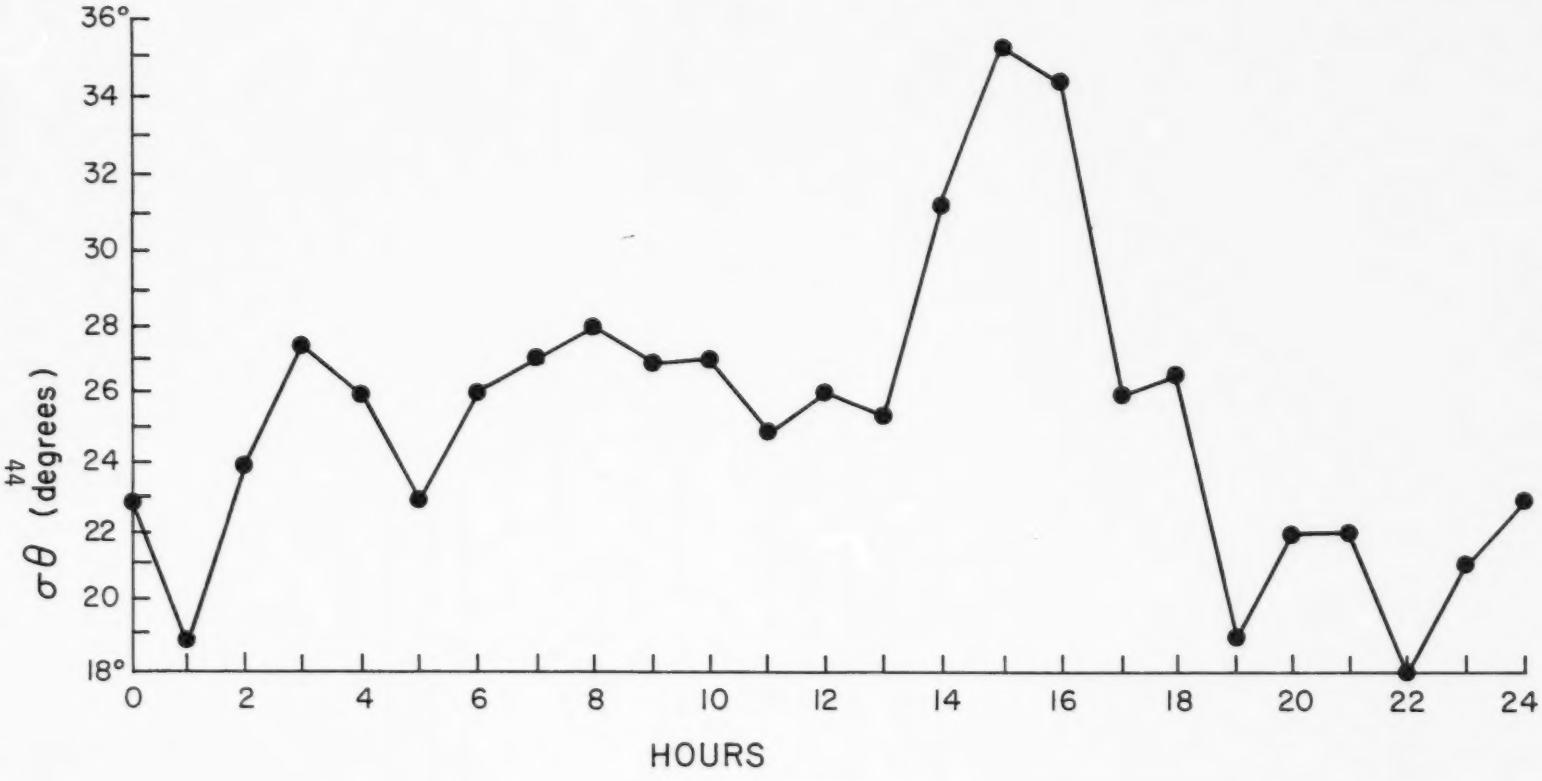

Figure 15. Median Hourly Gustiness, σ_θ, for Deposition Velocity Experiments. Pennsylvania Forest Site, August, 1979. (Note the non-zero base line)

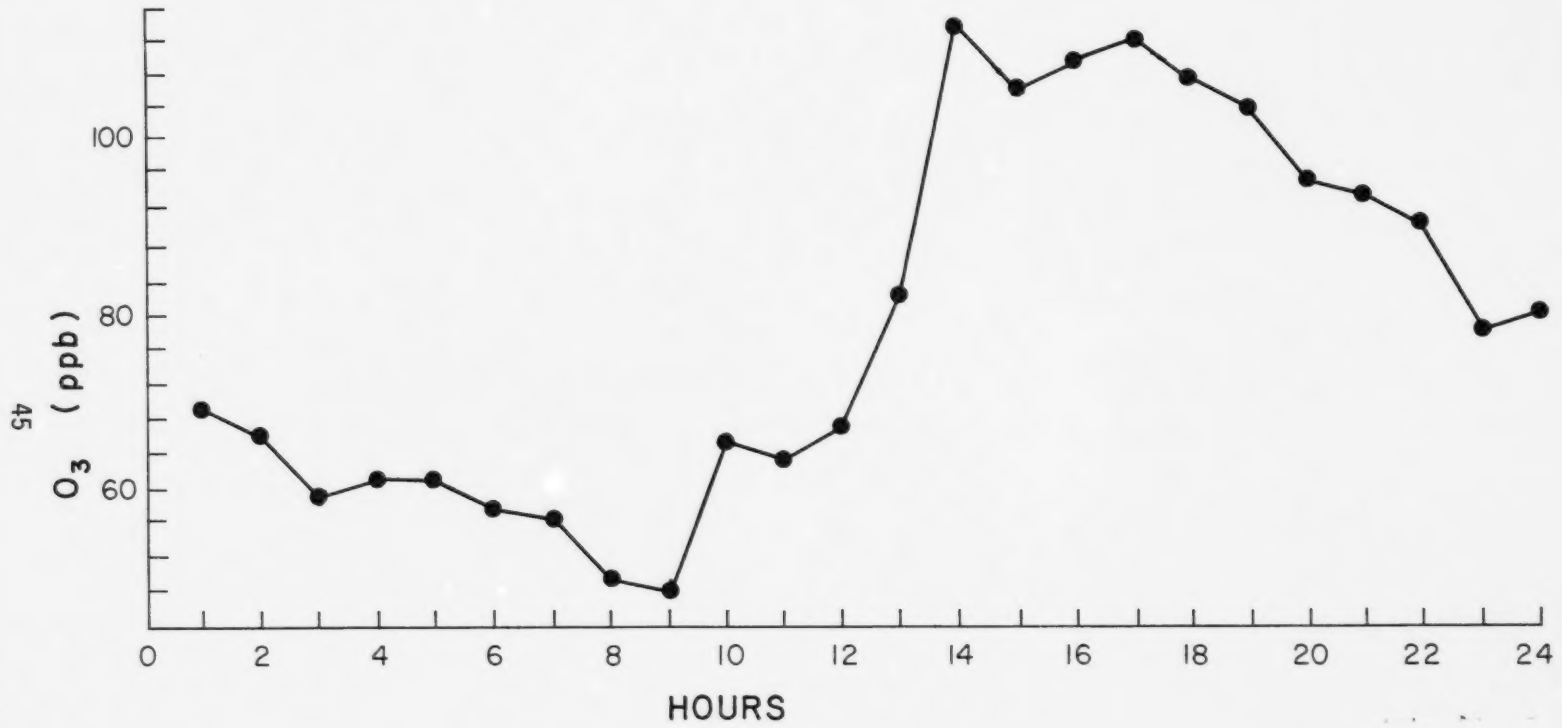

Figure 16. Median hourly Average O_3 Mixing ratio for Deposition Velocity Experiments. Pennsylvania Forest Site, August, 1979. (Note the non-zero O_3 base line)

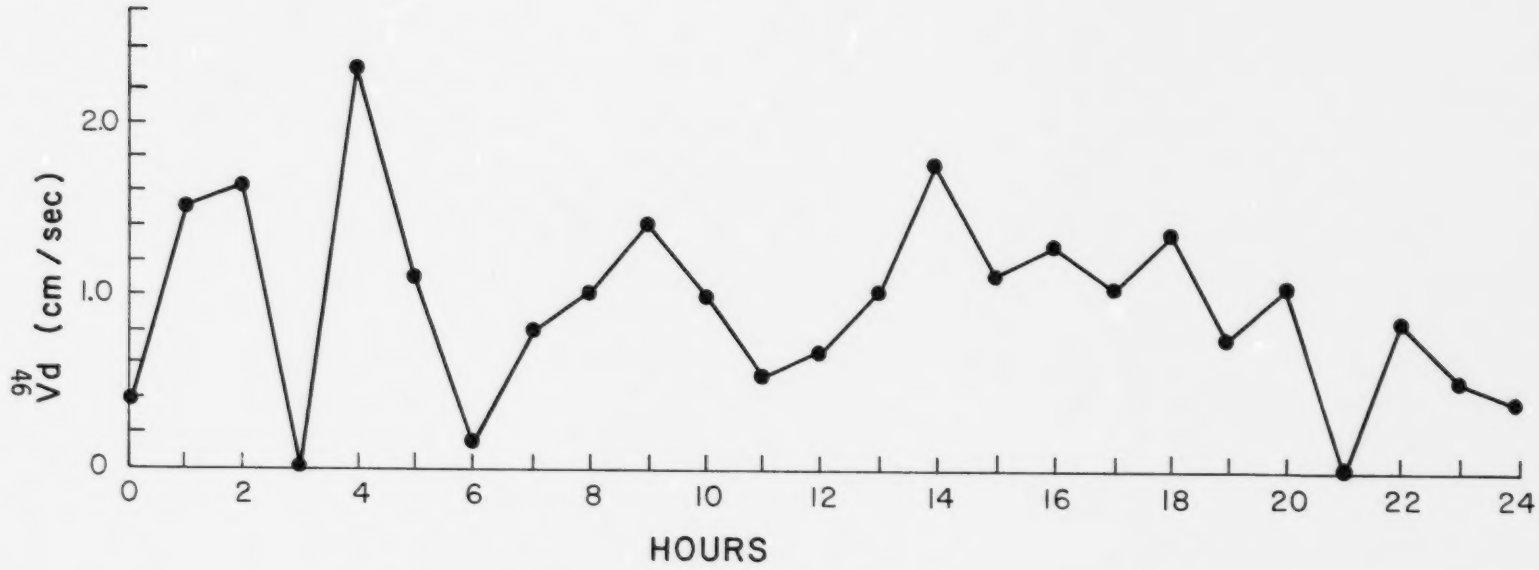

Figure 17. Median hourly values of Deposition Velocity. Pennsylvania Forest Site. August, 1979.

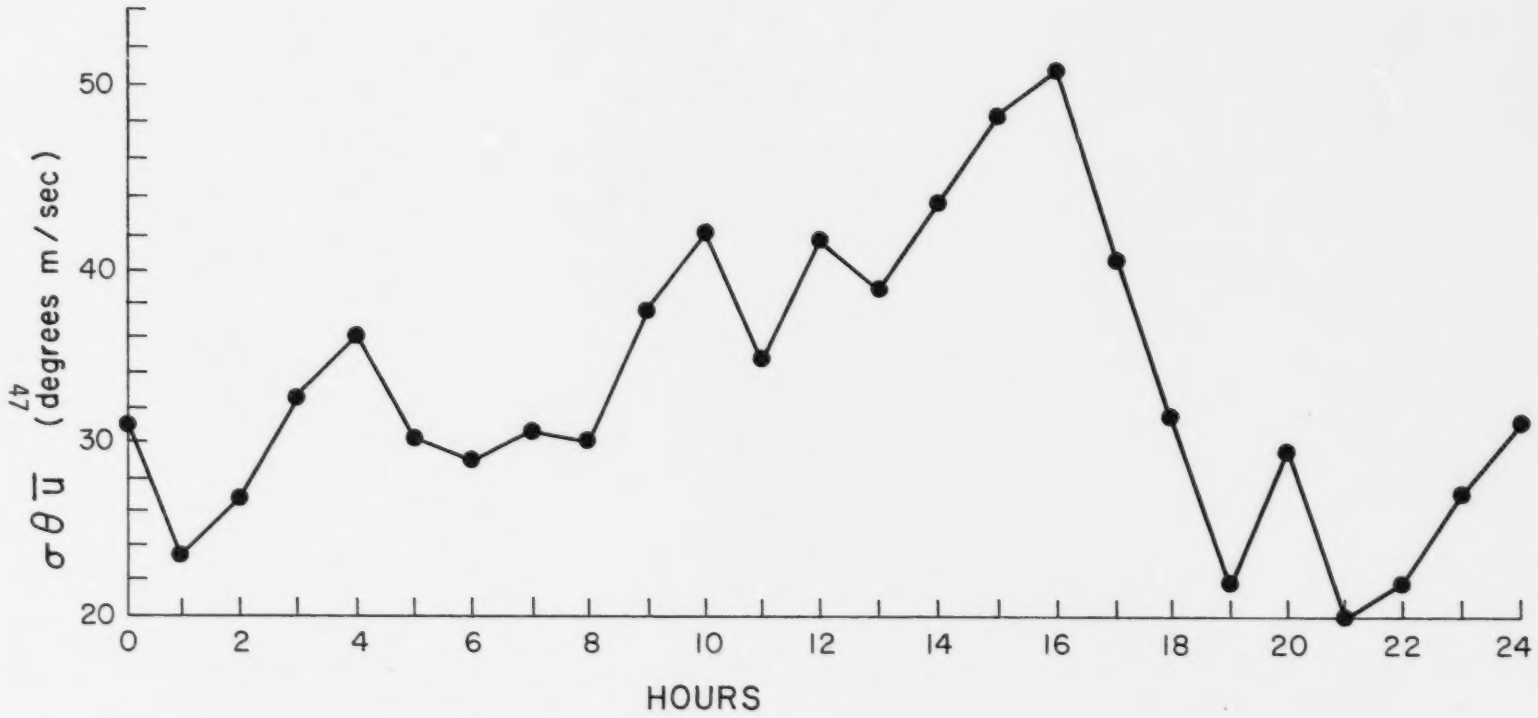

Figure 18. Median Hourly Values of Gustiness Parameter, $\sigma_\theta \bar{u}$. Pennsylvania Forest Site, August, 1979. (Note the non-zero base line)

The meteorological parameters that were investigated included measurements of temperature gradient along the tower between 20 m and 22.6 m and σ_θ at 20.9 m and 32 m, along with calculations of heat flux and the Obukhov scale length. These several parameters, although they are not all independent variables, each indicated turbulent or non-stable conditions. For the temperature gradient measurements only 5% of the hourly average gradients showed inversion lapse rates. This is in contrast to the expected forest model (Geiger, 1965) in which the forest canopy serves as a nocturnal radiating surface. This would establish a nighttime radiation inversion and stable conditions above the model forest. Such a pattern was not observed in the Pennsylvania experiment, when, as mentioned above, only 5% of the total observations showed inversion conditions through the first 2.6 m above the canopy.

The measurements of σ_θ above the canopy also indicate that stable flow with low values of gustiness were not characteristic of the Pennsylvania experiment. If a σ_θ value of 5° or less is used as an indication of "slightly" or "moderately" stable conditions, as suggested by Gifford (1968), less the 5% of the Pennsylvania 30-min averages at 32 m (12 m above the canopy) fell into the stable class. At the lower wind direction sensor, 20.9 m or 0.9 m above the average canopy, less than 2% of the 30-min averages were stable. If the σ_θ value is extended to 10° to include Gifford's (1968) neutral class 7% of the 20.9 m data and 16% of the 32 m data fall into a neutral and stable classification. As expected these lower σ_θ values occurred almost exclusively at night, after 1800 and before 0800 EDT. Thus the σ_θ observations are in agreement with the lapse rate data by indicating predominantly unstable flow conditions.

During the calculation program for V_d, values are obtained for the heat flux and for the Obukhov length. Since both of these variables depend on the temperature gradient it is not surprising that both were indicative of unstable flow conditions.

In addition to a careful reappraisal of the meteorological conditions of the Pennsylvania forest experiment we have also looked in detail at the O_3 concentration field, its variations and the possible impact on the measurement program. The O_3 field as it moved past the forest tower sampling site had frequent periods when the concentration was several times

the typical tropospheric background of 30 to 50 ppb. Since these summer experimental periods were done during times of general photochemical pollution, high O_3 concentrations were not unexpected; however these are also situations where the O_3 in the boundary layer is probably not in chemical equilibrium with the forest canopy. As mentioned previously a basic assumption of the gradient profile method for determining V_d is the existence of an equilibrium O_3 and meteorological profile above the canopy. The wind fetch across the forest was 1.2 to more than 1.6 km (Quarles, et al., 1981) and should have been sufficient to establish equilibrium (Droppo and Hales, 1976). However the turbulent boundary layer and the highly inhomogeneous O_3 field raise considerable question as to how often the O_3 profile was sufficiently in equilibrium to meet the requirements of the O_3 V_d determination. Figure 19 is a time series of O_3 mixing ratio at the forest site between 15 m and 32 m for the period 1200 EDT to 2000 EDT on August 14, 1979. Individual 5-minute average O_3 mixing ratio values are plotted on this figure in the same time sequence as they were measured. The isolines are an attempt to depict the short-term O_3 concentration trends during this experimental period. This was a period when the wind was across the forest and when a more or less stable O_3 profile was expected. This pattern clearly shows a series of high and low concentration eddies moving past the tower. A high concentration eddy developed between about 1200 and 1330 EDT and then gave way to a low concentration period centered around 1500 EDT. High concentrations occurred again about 1630 EDT followed by a period of more or less gradual decrease through 2000 EDT.

Figure 20 shows an O_3 time series for a nighttime period from 0100 through sunrise to 0900 on August 18, 1979. Although this O_3 pattern is somewhat more regular than the convective afternoon period shown in Figure 19, there are still considerable changes occurring in the pattern on a relatively short-term basis. In addition, the changes are not necessarily uniform from layer to layer as shown by the fact that centers of both high and low concentrations could identified, such as at 0130, 0300, and 0830. Periods of considerable concentration gradient are quite evident in Figure 20 such as that from 0500 to 0600 when concentrations decreased by about 10 ppb at all sampling levels.

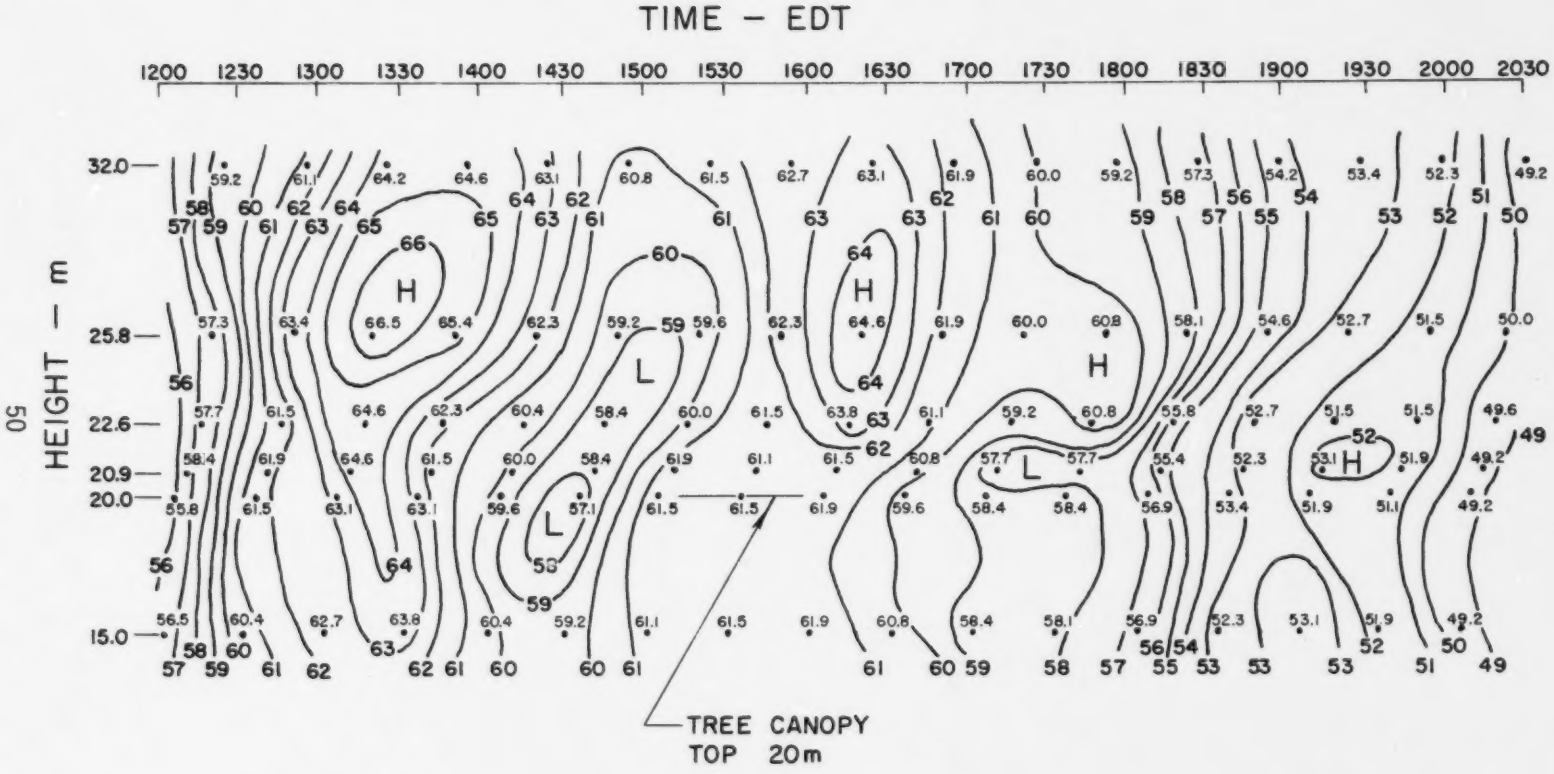

Figure 19. Time series of O_3 mixing ratio profiles between 15 and 32 m,. Pennsylvania Forest Site, 1200-2000 EDT, August 14, 1979.

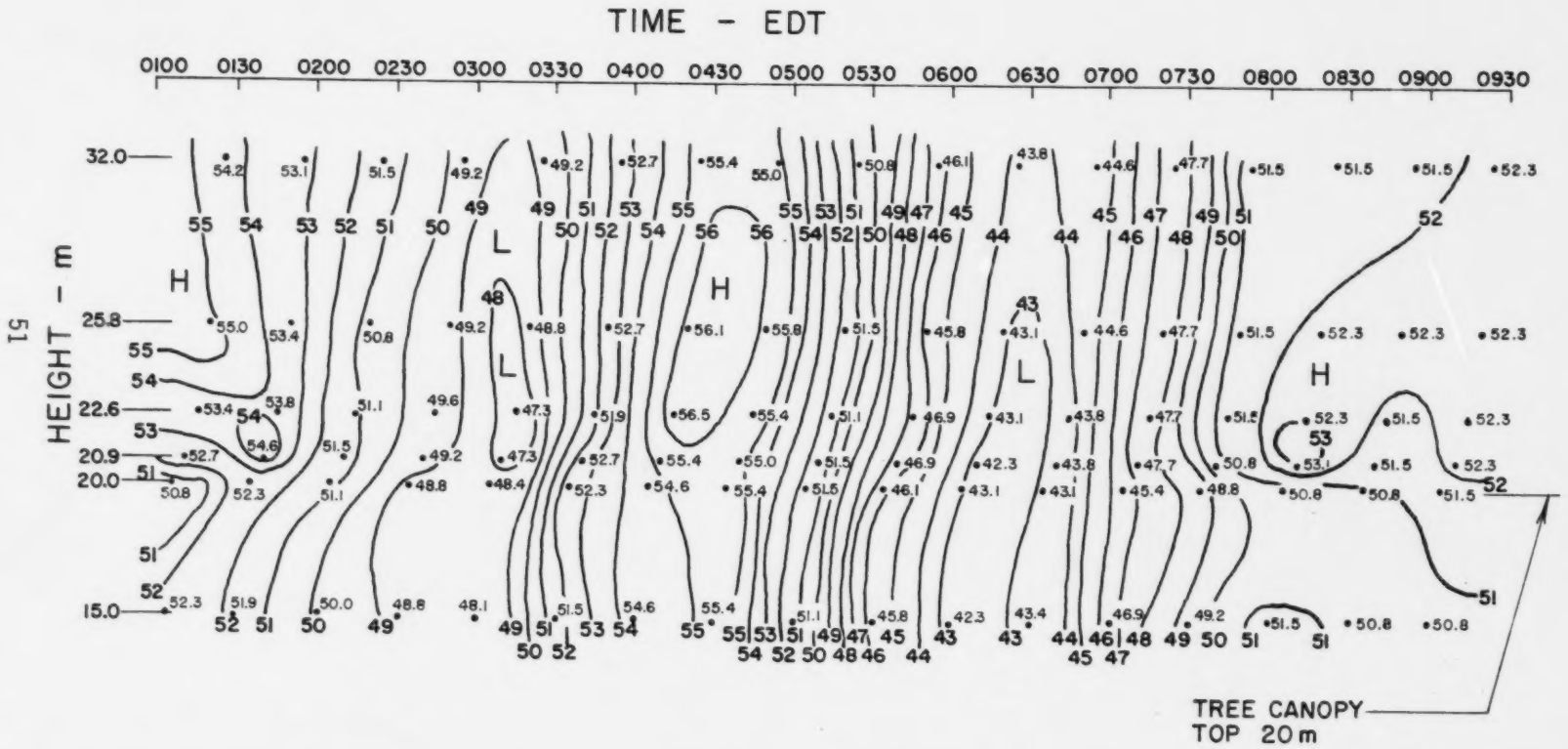

Figure 20. Time series of O_3 mixing ratio profiles between 15 and 32 m. Pennsylvania Forest Site, 0100-0900, EDT, August 14, 1979.

The high and low concentration centers shown in Figures 19 and 20 seem to be the type of pattern that would be produced by local formation and scavenging processes. These could be due to photochemical formation and scavenging processes during the daytime and to scavenging reactions at night. The local air mass typically contained significant concentrations of hydrocarbons and nitrogen oxides which would favor O_3 formation and destruction processes. The high daytime median concentrations as shown by Figure 16 is a clear indication of significant photochemical O_3 formation. This type of pattern was not characteristic of either the Illinois or Pullman experiments. In addition the relatively high concentration of leaf surface area may also play a role in O_3 scavenging as noted in the model studies of Shreffler (1978).

This more detailed examination of O_3 patterns over the Pennsylvania forest canopy seems to show that the O_3 concentration regime was in general not in long term equilibrium within the surface layers immediately above the canopy. As indicated above, there are, apparently, at least 2 reasons for this situation. First, active formation and scavenging of O_3 took place over the forest and significantly affected the O_3 pattern. The results were relatively short term cycles of concentration fluctuations and a lack of an established, consistent gradient over the canopy. Secondly, the flow over the canopy was typically an unstable turbulence regime which increased the variability and the difficulty in making V_d estimates from tower profiles. The increased roughness from the forest canopy and its large leaf surface area also may have been factors. During these detailed examinations of various aspects of the experiment additional calculations of V_d were made and compared with the original calculations used as a basis for Figure 17 and with the low crop V_d models. In general the detailed calculations showed V_d values 1 to several times higher than would have resulted from the previous crop experiments. Thus we have concluded the O_3 V_d values that are applicable to the Pennsylvania forest situation are generally higher than occur over more uniform, low crop lands. Shreffler (1978) has also concluded that values of V_d over a forest canopy can be 2 to 3 times as large as might be found over grass or other low vegetation. In addition, the persistence of a turbulence layer over the forest at night increased the total daily deposition by maintaiing an active transport to the canopy during the night.

MODEL APPLICATIONS

Estimates of V_d values for SO_2 on a regional basis have been made by Sheih, et al. (1979). These V_d estimates are based on approximations of Obukhov lengths, surface roughness, and surface resistance to deposition. The resulting values of V_d for SO_2 were calculated as a function of Pasquill (1962) stability class.

For models dealing with O_3 the present results sum to offer a relatively simple but still strongly empirical V_d modeling scheme through a relationship to $\sigma_\theta \bar{u}$. A starting point for estimating V_d for O_3 can be the general relationship described from the low crop experiments.

$$V_d = 0.0322(\sigma_\theta \bar{u})^{0.79}$$

Values of $\bar{u}$ can be obtained from either observed or forecast wind conditions. Where National Weather Service winds are used a correction from the standard observation height of 7 to 10 m to a height more appropriate to deposition velocity measurements of 1 - 2 m can be made using the power law wind profile

$$\frac{u_1}{u_2} = \left(\frac{z_1}{z_2}\right)^b$$

where b is a function of stability and equal to about 0.10 in unstable conditions, 0.15 in neutral, and 0.3 to 0.5 in stable conditions (Sutton, 1953). Estimates of σ_θ for use in the V_d estimate can be obtained by first estimating the applicable stability class from synoptic weather conditions as suggested by Pasquill (1962) or Turner (1964) and then applying a relationship between σ_θ and stability class. The relationship between these 2 variables as given by Gifford (1968) is shown in Table 2.

The results as given above for V_d as a function of $\sigma_\theta \bar{u}$ appears to be applicable to areas with relatively low crops such as the grain and soybeans over which the experiments were performed. Since these values of

Table 2. Values of $\sigma\theta$ as a Function of Pasquill Stability Class.*

Stability	Description	(degree)
A	Extremely Unstable	25
B	Moderately Unstable	20
C	Slightly Unstable	15
D	Neutral	10
E	Slightly Stable	5
F	Moderately Stable	2

*From: Gifford, F.A. Jr., Chapt 3 in: Meteorology and Atomic Energy, D.H. Slade, ed. USAEC, Div. Tech. Information, Oak Ridge, Tenn. 1968.

V_d are generally similar to the findings over low grass or other vegetation by Garland and Derwent (1979) in England and by Droppo and Doran (1979) in Washington State, the basic relationship seems reasonable. For significantly rougher surfaces such as forests the experimental results are not clear cut, as noted in the earlier discussion of the Pennsylvania forest studies. Qualitatively, a value for the O_3 V_d for forest areas might be estimated to be about 2 or 3 times the value estimated for similar conditions over a low crop surface. No data are available for water surfaces, for very rough urban areas, or dry sparsely vegetated desert areas.

CHAPTER 5

SUMMARY AND CONCLUSIONS

The previous chapters have described the principal objectives of this research program to be: (1) to carry out experiments that would permit the estimation of ozone deposition rate and ozone flux and (2) to analyze the possibility of relating ozone deposition velocity to a model based on meteorological variables. The purpose of the latter objective was to develop a "field-use-oriented" model correlating deposition velocity and easily measureable meteorological parameters. Then such a model could be used as input to air pollution transport and diffusion calculations.

This research was conducted at Robinson, Illinois in July-September, 1977, in Pullman, Washington from April to July, 1978 and near Lancaster, Pennsylvania in August 1979. These several studies provided a significant amount of data and the results have been summarized here. The Pennsylvania data were taken over an oak forest with a 20 m canopy height. It was determined that the forest results differed significantly from the results of the crop surface experiments.

The micrometeorological profile method was used as the experimental technique for the estimation of ozone V_d and ozone flux at the reference height of one meter above the crop surface. The Illinois data were obtained over a soybean crop which was about 75 cm high and growing actively in July, 1977 while in September it was a mature growth stage about 95 cm high. The Robinson, Illinois field was essentially flat. The weather in Illinois was characterized by strong daytime heating and considerable convective instability. The study site in Pullman, Washington had a mixed growth of grain, grass and weeds in active growth phase and the height of the crop was about 30 cm. The Pullman site was in a shallow valley with the axis of the valley along the line of the prevailing

southwest wind. The spring and early summer weather in Pullman, Washington was generally windy with limited convective instability.

The Pennsylvania forest experiment produced data that was not as readily interpreted as the Illinois and Pullman crop surface experiments. The top of the forest canopy did not, apparently, develop a strong diurnal pattern of nightime stability and daytime turbulence and there was a great deal of scatter in the values of all the calculated parameters. On the basis of median values of the various parameters the boundary layer over the canopy was determined to be characteristically unstable and turbulent. Median values of V_d were about 1 cm/sec with no significant diurnal cycle. Although the gustiness parameter $\sigma_\theta \bar{u}$ or G had an apparent diurnal cycle with maximum median values in the late afternoon, nighttime median values were also relatively large. The correlation between V_d and G was much lower than for the crop experiments. It should also be noted that this experimental period was one with significant regional photochemical ozone formation. To what extent this fact affected the results is unknown.

We do not believe that definitive conclusions can be drawn about V_d patterns over forest areas on the basis of this set of experimental data.

At the sites in Illinois and Pullman the vegetation characteristics were generally uniform for several hundred meters in the direction of the prevailing wind. There is no evidence that the terrain features adversely affected the profile measurements. The ozone dry deposition velocity and ozone flux were calculated using only those profiles that were recorded during the time-periods when the wind fetch was from a suitable sector.

The recorded profiles of wind speed, temperature and ozone concentrations were considered for an averaging period of 30 minutes. A graphical procedure was followed in obtaining the average profile for ozone concentration during the 3-minute averaging period. A similarity between the transfer of heat and the transfer of pollutant was assumed in relation to ozone V_d and ozone flux estimates. The ozone concentrations in these cropland experiments were indicative of "natural" or background conditions rather than urban area photochemistry. This was perhaps a significant difference relative to the forest experiment.

The experimental field data from Illinois and Pullman show that there is a general correspondence between the three experimental periods and the

two sites. Daytime values of V_d averaged 0.6 cm sec^{-1} with a standard deviation of 0.17 cm sec^{-1}. At night V_d values were in the general range from less than 0.1 to 0.3 cm sec^{-1} with some higher values when the nighttime winds were especially strong.

The daytime value of ozone V_d of 0.6 cm sec^{-1} is similar to recent values published by Garland and Derwent (1979) in England, and Droppo and Doran (1979) in the United States. The nighttime average of 0.2 cm sec^{-1} measured at both Robinson, Illinois and Pullman, Washington is comparable with the nighttime V_d average 0.29 cm sec^{-1} reported by Garland and Derwent (1979). Thus, the value of ozone V_d does not seem to be particularly sensitive to the underlying surface. This is not the case for other air pollutants, and in particular SO_2.

The daytime average ozone flux determined from crop land field study data is around 6×10^{11} molecules cm^{-1} sec^{-1}, and the nighttime flux is about 1.5×10^{11} molecules cm^{-2} sec^{-1}. The ozone flux reported by other investigators is in the general range of 1×10^{11} molecules cm^{-2} sec^{-1} to 6×10^{11} molecules cm^{-1} sec^{-1} (Galbally, 1971).

From the basic considerations of the micrometeorology of the boundary layer, we would expect V_d to generally related to the product G of lateral wind gustiness, σ_θ, and the mean wind, $\bar{u}$. In the WSU experiments at the two sites, acceptable statistical relationships between ozone V_d and G were obtained as follows:

Robinson, IL: July, 1977: $V_d = 0.0339(G)^{0.84}$

Sept., 1977: $V_d = 0.0241(G)^{0.78}$

Pullman, WA: April/May, 1978: $V_d = 0.0406(G)^{0.76}$

where $G = \sigma_\theta \bar{u}$ (deg ms^{-1}).

Although there are some differences between these three power law regressions that may be due to differences in the surfaces, they are still similar and have been combined into a single power law regression, namely,

$$V_d = 0.0322(G)^{0.79}$$

This expression could be used to derive values of V_d from estimates of σ_θ and $\bar{u}$ for a variety of crop land surfaces and sites.

For the Pennsylvania forest site, values of V_d were not well correlated with G. It is believed that the V_d estimates showed relatively large fluctuations because the O_3 profiles were not close enough to equilbrium with the canopy surface. It is suggested that this resulted from local formation and scavenging processes because of the influences of local and regional photochemical air pollutants. It appears from a subjective review of the forest site data that the model developed from the low crop experiments underestimates values of V_d for the forest by 50% or more.

The application of these results to transport model calculations was a principal objective of this research and it is believed that the results described above provide some reasonable progress toward this goal. For large scale transport and in most model studies it will be necessary to estimate values of σ_θ and $\bar{u}$ from the prevailing meteorological conditions. Values of $\bar{u}$ can be obtained directly from the observed or forecast wind field. Estimates of σ_θ can be obtained from an estimate of surface layer stability and the relationships between stability and σ_θ given by Gifford (1968). The stability classes can be determined from general weather conditions using either the relations described by Pasquill (1962) or Turner (1964).

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APPENDIX

Table 1. Ozone deposition velocity and micrometeorological data, July 1977.

Site: Robinson, Illinois
Period: 1555 hours, July 24, to 1025 hours, July 26, 1977.

Time (hours)	V_d	$\sigma_\theta \bar{u}$	C	F	σ_θ	$\bar{u}$
07-24-77						
1555-1625	0.70	42.77	62.5	10.8	18.0	238.6
1625-1655	0.60	25.54	57.3	8.4	16.4	155.7
1655-1725	0.43	25.78	57.4	6.1	16.4	157.2
1725-1755	0.39	13.81	63.0	6.0	11.0	125.5
1755-1825	0.40	14.00	62.9	6.2	11.0	127.2
1825-1855	0.40	17.18	55.4	5.4	12.3	129.6
1855-1925	0.62	23.37	48.2	7.4	13.1	178.4
1925-1955	0.48	16.20	44.5	5.2	11.5	140.8
1955-2025	0.20	7.66	40.3	2.0	8.8	87.0
2025-2055	0.27	12.98	39.6	2.6	9.0	144.2
2225-2255	0.15	14.05	41.7	1.5	11.3	124.3
2255-2325	0.20	12.14	42.7	2.1	11.9	102.0
2325-2355	0.49	19.60	47.4	5.7	12.2	160.6
2355-0025	1.26	13.08	54.3	3.5	10.1	129.5
07-25-77						
0025-0055	0.34	18.18	55.3	4.6	11.5	158.0

Table 1. (Continued).

Time (hours)	V_d	$\sigma\theta\bar{u}$	C	F	$\sigma\theta$	$\bar{u}$
0055-0125	0.22	18.90	55.2	2.9	11.3	167.2
0125-0155	0.28	17.66	55.5	3.8	11.4	154.9
0155-0225	0.16	13.67	55.5	2.2	11.9	114.9
0225-0255	0.09	14.99	54.4	1.3	12.5	119.9
0255-0325	0.16	10.29	52.4	2.0	12.0	85.7
0325-0355	0.25	23.04	49.9	3.1	12.7	181.4
0355-0425	0.04	7.77	44.1	0.4	8.2	94.8
0425-0455	0.03	4.65	31.4	0.2	10.3	45.1
07-25-77						
0625-0655	0.16	7.95	28.3	1.1	11.2	71.0
0655-0725	0.38	7.75	30.5	2.8	10.1	76.7
0725-0755	0.33	13.97	32.2	2.6	13.8	101.2
0755-0925	0.04	7.77	33.7	0.3	14.7	52.8
0925-0955	0.66	21.26	27.0	4.4	12.6	168.7
0955-1025	1.01	22.96	38.3	7.7	11.8	194.5
1025-1055	0.62	23.74	47.8	7.3	11.4	208.2
1055-1125	0.62	17.88	48.5	7.3	10.7	167.0
1125-1155	0.61	16.59	44.9	6.8	11.6	143.0
1155-1225	0.44	15.98	43.5	4.7	12.9	123.9
1225-1255	0.41	12.29	40.5	4.1	11.1	110.7
1255-1325	0.34	14.49	41.7	3.5	14.8	97.9
1325-1355	0.47	14.09	41.0	4.8	14.7	95.8
1355-1425	0.43	26.36	46.5	4.9	27.7	95.1

Table 1. (Continued)

Time (hours)	V_d	$\sigma_\theta \bar{u}$	C	F	σ_θ	$\bar{u}$
1425-1455	1.00	40.97	48.5	11.9	14.9	274.9
1455-1525	0.50	12.09	43.5	5.3	19.5	6.20
1525-1555	0.39	19.09	44.5	4.3	16.2	117.8
1555-1625	0.89	37.10	44.6	9.7	13.3	278.9
1625-1655	0.67	36.27	48.7	8.0	13.5	268.7
1655-1725	0.68	38.54	50.6	8.5	12.8	301.0
1725-1755	0.65	31.35	41.3	8.2	12.2	256.0
1755-1825	0.60	37.91	50.3	7.4	13.2	291.6
1825-1855	0.60	31.42	46.5	7.4	10.4	302.1
1855-1925	0.60	39.86	43.1	7.4	12.7	235.1
1925-1955	0.60	29.02	38.9	7.4	11.8	245.9
1955-2025	0.55	37.45	42.3	5.7	12.0	312.0
2025-2055	0.47	27.84	40.3	4.7	12.4	224.5
2055-2125	0.39	32.13	32.5	3.1	12.7	234.4
2125-2155	0.57	25.92	30.9	4.3	11.6	223.4
2155-2225	0.50	25.10	33.3	4.1	11.2	224.1
2225-2255	0.69	26.31	30.4	5.2	11.7	224.8
07-26-77						
0125-0155	0.31	13.61	22.0	1.7	10.2	133.4
0155-0225	0.19	8.95	20.5	0.9	10.1	88.9
0225-0255	0.31	6.07	19.0	1.5	7.8	77.8
0255-0325	0.33	3.58	16.7	1.4	6.4	55.9
0325-0355	0.20	3.48	15.0	0.7	7.7	45.2

Table 1. (Continued)

Time (hours)	V_d	$\sigma\theta\bar{u}$	C	F	$\sigma\theta$	$\bar{u}$
0525-0555	0.29	7.96	15.1	1.1	8.9	89.4
0555-0625	0.29	9.24	15.0	1.1	9.2	100.4
0855-0925	0.65	22.85	35.0	6.8	10.8	211.5
0925-0955	0.63	28.49	36.4	7.8	10.6	268.7
0955-1025	0.60	30.21	38.0	8.4	12.3	245.6

V_d: Dry deposition velocity (cm sec^{-1})
$\bar{u}$: Turbulence parameter (deg meters sec^{-1})
C: Ozone concentration at 100 cm above the crop surface (ppb)
F: Ozone flux at 100 cm above the crop surface (10" molecules $cm^{-2}sec^{-1}$)
_: Standard deviation of horizontal wind direction fluctuation (deg)
$\bar{u}$: Horizontal wind speed (cm sec^{-1})

Table 2. Ozone deposition velocity and micrometeorological data, September 1977.

Site: Robinson, Illinois
Period: 1430 hours, September 9, to 1630 hours, September 11, 1977.

Time (hours)	V_d	$\sigma\theta\bar{u}$	C	F	$\sigma\theta$	$\bar{u}$
09-09-77						
1430-1500	0.70	25.0	76.6	13.2	11.8	211.8
1500-1530	0.60	23.0	77.7	11.5	10.6	216.9
1530-1600	0.75	35.0	83.1	15.3	9.5	368.4
1600-1630	0.42	42.0	91.2	9.4	10.3	408.0
1630-1700	0.52	27.0	98.9	12.6	9.7	278.0
1700-1730	0.34	37.0	96.1	8.0	11.2	330.0
1730-1800	0.46	20.0	82.8	9.3	9.7	206.0
1800-1830	0.46	10.0	70.7	8.0	7.1	141.0
1830-1900	0.14	10.00	64.4	2.2	6.1	164.0
1900-1930	0.43	43.0	59.7	6.3	18.2	236.0
1930-2000	0.14	17.0	57.2	1.9	7.6	224.0
2000-2030	0.16	21.0	55.6	2.2	7.8	269.0
2030-2100	0.16	21.0	54.5	2.1	8.8	238.6
2100-2130	0.08	20.0	52.2	1.0	9.6	208.8
2130-2200	0.06	18.0	49.5	0.7	12.1	148.0
2200-2230	0.04	15.0	43.6	0.4	20.1	74.6
2230-2300	0.05	10.0	39.5	0.5	27.5	36.3
2300-2330	0.06	5.0	33.0	0.5	0.6	79.5
2330-0000	0.10	1.0	21.0	0.5	1.9	56.8

Table 2. (Continued)

Time (hours)	V_d	$\sigma\theta\bar{u}$	C	F	$\sigma\theta$	$\bar{u}$
1100-1130	0.68	45.0	54.0	9.0	22.5	200.0
1130-1200	0.60	62.0	55.0	8.1	23.2	267.2
1200-1230	0.56	43.0	55.0	7.6	16.9	254.4
1230-1300	0.50	65.0	57.2	7.0	19.9	326.6
1300-1330	0.46	47.0	57.7	6.5	16.6	283.1
1330-1400	0.44	60.0	55.7	6.0	18.3	327.8
1400-1430	0.62	61.0	56.6	8.6	18.8	324.7
1430-1500	0.52	63.0	58.4	7.5	21.8	288.9
1500-1530	0.64	51.0	60.6	9.5	15.8	322.8
1530-1600	0.60	53.0	62.6	9.2	18.6	284.9
1600-1630	0.50	45.0	64.8	8.0	16.5	272.7
1630-1700	0.40	40.0	66.3	6.5	14.5	275.8
1700-1730	0.36	37.0	67.0	5.9	14.4	256.9
1730-1800	0.26	35.0	66.7	4.3	12.5	280.0
1800-1830	0.20	25.0	62.3	3.1	9.7	257.7
1830-1900	0.10	10.0	52.1	1.3	5.7	175.4
1900-1930	0.06	5.0	44.5	0.7	3.0	166.7
1930-2000	0.06	3.0	36.0	0.5	3.9	76.9
2000-2030	0.05	3.0	26.0	0.3	2.2	131.6
2030-2100	0.04	5.0	22.0	0.2	8.8	56.7
2100-2130	0.02	2.5	19.0	0.09	8.6	29.0
2130-2200	0.02	6.0	17.0	0.08	10.2	58.4
2200-2230	0.06	7.0	12.0	0.18	7.0	99.0

Table 2. (Continued)

Time (hours)	V_d	$\sigma\theta\bar{u}$	C	F	$\sigma\theta$	$\bar{u}$
09-10-77						
0000-0030	0.06	2.0	18.0	0.3	2.5	78.2
0030-0100	0.07	1.1	17.0	0.3	2.2	48.2
0100-0130	0.04	2.0	15.0	0.2	3.5	56.2
0130-0200	0.02	1.1	13.0	0.06	2.3	46.3
0200-0230	0.02	1.5	14.0	0.07	3.5	41.8
0230-0300	0.02	1.5	16.0	0.08	9.0	16.6
0300-0330	0.02	1.5	14.0	0.07	13.2	11.3
0330-0400	0.04	1.5	14.0	0.14	13.2	11.3
0400-0430	0.03	3.0	13.0	0.10	36.1	8.3
0430-0500	0.04	4.5	9.0	0.09	31.9	14.1
0500-0530	0.02	7.0	7.0	0.03	32.7	21.4
0530-0600	0.03	6.0	7.0	0.05	13.2	45.2
0600-0630	0.04	2.0	8.0	0.08	11.0	18.2
0630-0700	0.06	2.0	12.0	0.18	10.5	19.0
0700-0730	0.08	2.0	16.0	0.31	7.6	26.2
0730-0800	0.20	5.0	20.0	1.0	6.5	78.4
0800-0830	0.40	7.0	26.0	2.6	9.9	70.7
0830-0900	0.64	10.0	29.0	4.6	11.9	84.0
0900-0930	0.70	15.0	31.0	5.3	11.5	130.4
0930-1000	0.80	30.0	32.0	6.3	18.4	163.0
1000-1030	1.00	26.0	34.0	8.4	18.5	140.5
1030-1100	0.90	35.0	40.0	8.8	24.4	143.4

Table 2. (Continued)

Time (hours)	V_d		C	F		$\bar{u}$
2230-2300	0.07	3.0	15.0	0.26	5.1	58.7
2300-2330	0.05	3.0	14.0	0.17	7.9	37.7
09-11-77						
0530-0600	0.04	1.1	10.0	0.10	5.1	21.9
0600-0630	0.03	1.1	11.0	0.08	5.4	20.4
0630-0700	0.05	1.5	12.0	0.15	17.4	8.6
0700-0730	0.06	2.0	14.0	0.21	13.9	14.3
0730-0800	0.12	4.0	18.0	0.53	16.2	24.7
1300-1330	0.48	65.0	73.7	8.7	29.3	221.4
1330-1400	0.45	60.0	74.8	8.3	35.6	168.4
1400-1430	0.50	55.0	75.3	9.2	27.3	201.2
1430-1500	0.60	55.0	76.0	11.2	22.0	250.0
1500-1530	0.64	60.0	77.0	12.1	32.2	186.3
1530-1600	0.64	61.0	77.0	12.1	27.0	225.9
1600-1630	0.66	61.0	79.0	12.8	21.0	290.8

V_d: Dry deposition velocity (cm sec^{-1})
$\bar{u}$: Turbulence parameter (deg meters sec^{-1})
C: Ozone concentration at 100 cm above the crop surface (ppb)
F: Ozone flux at 100 cm above the crop surface (10" molecules $cm^{-2}sec^{-1}$)
_: Standard deviation of horizontal wind direction fluctuation (deg)
$\bar{u}$: Horizontal wind speed (cm sec^{-1})

Table 3. Ozone deposition velocity and micrometeorological data, April 1978.

Site: USDA Farm, Pullman, Washington
Period: 1516 hours, April 22, to 0016 hours, April 25, 1978.

Time (hours)	V_d	$\sigma_\theta \bar{u}$	C	F	σ_θ	$\bar{u}$
04-22-78						
1516-1546	0.37	11.16	41.0	3.7	8.2	136.1
1546-1616	0.46	13.64	41.7	4.7	12.6	108.2
1616-1646	1.24	29.36	46.2	14.1	10.7	274.4
1646-1716	0.86	14.83	51.6	10.9	7.8	190.1
1716-1746	0.61	10.68	49.1	7.4	10.1	105.7
2046-2116	0.24	11.83	41.1	2.4	7.0	169.0
2116-2146	0.28	14.82	41.8	2.9	7.0	211.7
2146-2216	0.24	13.13	42.6	2.5	6.8	193.1
2216-2246	0.21	11.81	42.0	2.2	6.2	190.5
2246-2316	0.24	9.51	41.0	2.4	7.0	135.8
2316-2346	0.20	11.20	41.3	2.0	6.7	167.2
2346-0016	0.26	11.38	40.4	2.6	6.5	175.1
04-23-78						
0016-0046	0.18	8.99	29.8	1.8	6.6	136.2
0046-0116	0.28	12.86	39.0	2.7	6.8	189.1
0116-0146	0.18	10.52	37.5	1.7	6.9	152.4
0146-0216	0.17	8.24	35.9	1.5	7.4	111.3
0216-0246	0.23	9.01	36.4	2.1	8.4	107.3
0246-0316	0.13	7.20	36.9	1.2	8.8	81.8

Table 3. (Continued)

Time (hours)	V_d	$\sigma\theta\bar{u}$	C	F	$\sigma\theta$	$\bar{u}$
0316-0346	0.13	8.46	36.4	1.2	6.4	132.2
0346-0416	0.17	9.03	35.6	1.5	7.5	120.4
0416-0446	0.14	9.94	40.8	1.4	6.8	146.2
0446-0516	0.18	8.98	35.1	1.5	6.8	132.0
0516-0546	0.11	6.78	35.0	0.9	6.2	109.3
0546-0616	0.11	7.65	35.6	0.9	5.9	129.7
0616-0646	0.11	7.62	35.8	1.0	7.5	136.1
0646-0716	0.25	21.06	35.5	2.2	17.6	119.6
0716-0746	0.39	15.10	37.3	3.6	16.1	93.8
0746-0816	0.46	16.17	39.5	4.5	9.9	163.3
0816-0846	0.51	19.18	41.0	5.1	11.7	163.9
0846-0916	0.51	20.17	40.9	5.1	13.8	146.1
0916-0946	0.38	21.76	41.5	3.9	13.5	161.2
0946-1016	0.45	26.54	43.4	4.8	21.3	124.6
04-24-78						
0016-0046	0.08	3.35	36.8	0.7	8.4	39.8
0046-0116	0.12	4.24	36.6	1.1	8.0	53.0
0116-0146	0.02	1.68	37.2	0.2	7.9	21.2
0146-0216	0.02	2.95	37.4	0.2	8.5	34.7
0216-0246	0.02	4.10	37.6	0.1	8.3	49.4
0246-0316	0.07	4.61	36.9	0.6	8.1	96.9
0316-0346	0.08	4.36	35.6	0.7	8.0	54.5
0346-0416	0.06	4.33	35.0	0.5	0.7	61.8

Table 3. (Continued)

Time (hours)	V_d	$\sigma\theta\bar{u}$	C	F	$\sigma\theta$	$\bar{u}$
0416-0446	0.06	3.42	36.6	0.6	7.7	44.4
0446-0516	0.20	7.26	36.3	1.8	8.4	86.4
0516-0546	0.14	9.13	35.4	1.2	8.7	104.9
0546-0616	0.15	5.31	34.9	1.3	8.0	66.4
0616-0646	0.17	13.85	34.6	1.4	9.0	153.9
0646-0716	0.27	11.65	33.4	2.2	8.3	140.4
0716-0746	0.52	13.43	33.0	4.2	8.4	159.9
0746-0816	0.66	14.53	33.0	5.3	9.6	151.1
0816-0846	0.59	14.26	32.0	4.6	9.1	156.7
0846-0916	0.75	17.75	33.0	6.1	9.9	179.3
0916-0946	0.60	16.54	36.0	5.3	10.3	160.6
0946-1016	0.66	18.36	38.2	6.2	11.2	163.9
1016-1046	0.57	17.38	38.1	5.4	11.2	155.2
1046-1116	0.57	12.60	40.0	5.6	11.0	114.5
1116-1146	0.79	15.35	40.4	7.8	10.4	147.6
1146-1216	0.77	16.25	40.3	7.6	11.4	142.5
1216-1246	0.65	14.41	41.0	6.5	10.1	142.6
1246-1316	0.71	9.36	41.5	7.2	8.3	112.7
1316-1346	0.73	13.85	42.4	7.6	11.9	116.4
1346-1416	0.57	13.09	41.5	5.8	11.4	114.8
1416-1446	0.54	12.85	41.1	5.5	11.0	116.8
1446-1516	0.47	10.94	38.8	4.5	9.0	121.5
1516-1546	0.47	10.66	39.0	4.5	9.4	113.4

Table 3. (Continued)

Time (hours)	V_d		C	F		$\bar{u}$
1546-1616	0.47	10.92	38.4	4.4	8.7	125.5
1616-1646	0.47	9.36	37.7	4.4	8.5	110.1
1646-1716	0.47	10.74	35.8	4.1	8.7	123.4
1716-1746	0.47	8.92	34.8	4.0	7.6	129.2
1746-1816	0.47	6.43	31.4	3.6	7.6	84.6
1816-1846	0.47	5.12	28.8	3.3	6.6	77.5
1846-1916	0.16	5.25	24.7	1.0	6.8	77.2
1916-1946	0.29	8.37	29.0	2.1	7.7	108.7
1946-2016	0.31	10.71	27.7	2.1	8.3	129.0
2016-2046	0.29	9.28	27.2	1.9	7.9	117.5
2046-2116	0.29	12.87	28.5	1.9	8.9	144.6
2116-2146	0.19	9.14	27.6	1.3	8.2	111.4
2146-2216	0.14	7.21	27.9	0.9	8.5	84.8
2216-2246	0.06	3.60	28.9	0.4	5.5	65.4
2246-2316	0.11	3.84	29.1	0.8	6.2	61.9
2316-2346	0.11	3.85	30.0	0.81	5.3	72.6
2346-0016	0.11	2.36	30.5	0.8	6.2	38.0

V_d: Dry deposition velocity (cm sec^{-1})
$\bar{u}$: Turbulence parameter (deg meters sec^{-1})
C: Ozone concentration at 100 cm above the crop surface (ppb)
F: Ozone flux at 100 cm above the crop surface ($10^{"}$ molecules $cm^{-2}sec^{-1}$)
_: Standard deviation of horizontal wind direction fluctuation (deg)
$\bar{u}$: Horizontal wind speed (cm sec^{-1})